

# The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching Constituents from Cements and Concretes



# SCIENCE

# **The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on the Leaching of Constituents from Cements and Concretes**

**Hans A. van der Sloot<sup>1</sup>, David S. Kosson<sup>2</sup>, Andrew C. Garrabrants<sup>2</sup>, and Joshua Arnold<sup>2</sup>**

<sup>1</sup> Hans van der Sloot Consultancy  
1721 BV Langedijk, the Netherlands

<sup>2</sup> Vanderbilt University  
Civil and Environmental Engineering  
Nashville, TN 37235

Category III / Applied Research

EPA Contract No. EP-C-09-027

Work Assignment No. 3-07

Prepared for  
**Susan A. Thorneloe**  
U.S. Environmental Protection Agency  
Office of Research and Development  
National Risk Management Research Laboratory  
Air Pollution Prevention and Control Division  
Research Triangle Park, NC 27711

## **Acknowledgements**

This study was conducted under the United States Environmental Protection Agency (USEPA) Contract Number EP-C-09-27 coordinated by ARCADIS-US, Inc. (ARCADIS). Partial financial support was provided by the U.S. Department of Energy, Office of Environmental Management, under Cooperative Agreement Number DE-FC01-06W07053 entitled “The Consortium for Risk Evaluation with Stakeholder Participation III” awarded to Vanderbilt University.

The authors also thank Tim Taylor (USEPA Office of Resource Conservation and Recovery), Susan Thorneloe and Nick Hutson (USEPA Office of Air Quality, Planning, and Standards)) as well as Peter Kariher (ARCADIS) for their guidance and contributions during the development of this report.

## **Abstract**

Using available data from Europe and the United States (US), this report compares the leaching of portland cement-based materials that have been prepared with and without coal combustion fly ash. The objective of this report is to illustrate whether there is evidence *based on existing data* that the use of fly ash in cement and concrete products may result in increased leaching of constituents of potential concern (COPCs) compared to cement and concrete products that do not contain fly ash. Results of pH dependent leaching and cumulative release from monolith leaching, as described in the Leaching Environmental Assessment Framework (LEAF) are used for the evaluation. LEAF data is also compared with relevant single point leaching test data.

The available data suggest that the use of coal combustion fly ash in cement materials, for different combinations of fly ash source and usage rates, will not increase leaching of some constituents to levels greater than typical ranges for cement materials not containing fly ash. However, there are data limitations that preclude making broad-based claims for some usage rates and fly ashes including those resulting from changes in air pollution control at coal-fired power plants. Based on available data (31 cement mortar and concrete samples containing coal fly ash in comparison to 21 cement and mortar samples that did not contain coal fly ash), results indicate that some (and probably a large portion) of coal fly ashes currently being produced can be used in cement and concrete formulations without causing greater leaching of COPCs than observed from analogous cement materials not containing fly ash and without causing adverse environmental impacts. The range of fly ash sources and usage rates for cement materials with pH dependent and monolith leaching test data available is more limited than the full range of typical fly ash usage rates and typical fly ash leaching behavior. For example, fly ash substitution rates for cement of up to ca. 45 wt% is typical in US large commercial concrete applications, while the predominance of materials reported here have ca. 20-35 wt% fly ash substitution. In addition, the data evaluated in this report does not consider changes in leaching from cement-based materials that may occur if the characteristics of coal fly ash used in cement-based materials change in response to changes in air pollution control requirements at coal fired power plants.

The LEAF methodology, specifically including pH dependent and monolith leaching test data as a basis for evaluation, provides a more robust approach than single point leaching tests for evaluating the potential environmental impacts from use of coal fly ash in cement and concrete materials because LEAF considers the likely range of leaching pH over the lifecycle and the physical form of the materials (i.e., monolithic). Leaching of individual constituents from cement materials exhibits characteristic concentration as a function of pH responses. Future work is recommended using the LEAF methodology to evaluate coal combustion residues (CCRs) that are specifically marketed for use in producing cementitious materials and reflect changes occurring in air pollution control at coal-fired power plants. The focus of future work would be to confirm the findings from this report and to identify any materials, usage rates, or other conditions that might lead to release of COPCs that could be of concern to human health and the environment. This approach would support continued use of fly ash in cement and concrete products while ensuring protection of human health and the environment.

## **Executive Summary**

The objective of this report is to compare the leaching of portland cement-based materials that have been prepared with and without coal combustion fly ash to illustrate whether there is evidence that the use of fly ash in cement and concrete products may result in increased leaching of constituents of potential concern (COPCs) compared to cement and concrete products that do not contain fly ash. This report evaluates in a new context the leaching results obtained from studies carried out for other purposes, and as such, the observations and conclusions of this report should be considered indicative of performance but not inclusive of the full range of range of possible coal fly ashes used in cement and concrete, usage rates (fly ash can typically be up to 50 wt% of the dry mixture of cementitious materials), or leaching performance of the resulting materials.

In summary, the cement mortar and concrete data sets evaluated include the following:

- pH dependence leaching test results for 13 cement mortar and concrete samples without fly ash in the European Union (EU) data set, including one sample from Thailand, compared with 11 cement mortar and concrete samples prepared with fly ash, including one sample from Brazil and Chile. The specific sources and leaching characteristics (e.g., liquid-solid partitioning as functions of pH or liquid-to-solid ratio, rates of mass transport) of the fly ash used are unknown.
- Mass transfer leaching test results (monolith tests) for 21 cement mortar and concrete samples without fly ash in the EU data set, including one sample from Thailand, compared with 27 cement mortar and concrete samples prepared with fly ash. The specific sources and leaching characteristics of the fly ash used are unknown.
- pH dependence leaching test (Method 1313) and mass transfer leaching test results (Method 1315) for four cement mortar and concrete samples containing fly ash. The sources and leaching characteristics of the fly ashes (two types) used are known.
- Single extraction leaching test results (either synthetic acid precipitation or deionized water batch extraction) for one fly ash used at three rates (0- control, 30 and 50 wt% substitution for portland cement) and two additional fly ash samples at three usage rates (0 - control, 30 and 60 wt%). The sources of the fly ash are known but the fly ash leaching characteristics under relevant conditions are not known.

The following types of comparisons are made:

- The range of leaching performance for cement mortars and concrete predominantly from the EU formulated without fly ash is compared to EU cement mortars and concretes formulated with fly ash (10-30 wt% replacement of cement by fly ash) as a primary constituent. In this comparison, the leaching characteristics and specific origin (e.g., coal source, facility configuration, and handling processes) of the fly ash materials are not known although the fly ash was required to meet specifications according to EU standard EN 197-1. The 90 percent confidence intervals for observed leaching of constituents are provided for EU cement mortars

formulated with fly ash and the analogous mortars and concretes prepared without fly ash. Release levels are compared with Dutch regulatory criteria for construction products in service life. The 90 percent confidence intervals for EU cement mortars and concretes formulated with fly ash were used as the reference basis for comparison with the other (United States and Canada) data sets because this case represented the greatest number of independent samples.

- The range of leaching performance for a series of cement mortar samples prepared using typical slag cement mixtures using portland cement, slag and fly ash with different amounts of fly ash (23.5 – 55.8 wt% fly ash in the dry mixture) is compared to leaching from the fly ash used in the formulations alone. The 90 percent confidence intervals with respect to leaching from the EU cement mortars formulated with fly ash are included to place these comparisons in context to the EU dataset. The leaching of the fly ash used in samples from the Cement Barriers Partnership (CBP), a project supported by the United States Department of Energy (USDOE), is also compared to leaching of a broader set of fly ash samples.
- Leaching performance of a blended cementitious paste representative of solidification/stabilization (S/S) formulation and the fly ash used in that paste. The 90 percent confidence intervals from EU cement mortars and concrete formulated with fly ash are included to place these materials in context to the EU dataset.
- Results from testing several mortars using synthetic precipitation leaching procedure (SPLP) or deionized water are also compared with the 90 percent confidence intervals with respect to leaching from the EU cement mortars formulated with fly ash. US Environmental Protection Agency (USEPA) health based numbers (HBNs) are also included in this comparison to put the data sets in context with environmental risk thresholds.

Testing results from the Leaching Environmental Assessment Framework (LEAF) methods and analogous EU methods, specifically results from pH dependent and monolith leaching tests, were used as the basis for evaluation in this report. Leaching test results (pH dependence test and monolith test results) from 31 cement mortar and concrete samples containing coal fly ash are compared to leaching test results from 21 cement mortar and concrete samples that did not contain coal fly ash. In addition, results from testing of cement mortars and concrete samples using the Synthetic Precipitation Leaching Procedure (SPLP) and deionized water are compared with the broader set of results and HBNs.

Based on the evaluation of available data for the leaching of cement mortars and concrete with and without partial replacement of cement with coal combustion fly ash, the following observations can be made:

- The leaching behavior of individual constituents from cement mortars and concrete made with coal fly ash exhibits characteristic leaching behavior (e.g., the shape and general order of magnitude of the LSP curve is “systematic” for each COPC regardless of the details of the material) as a function of pH responses that are controlled by the cement chemistry.
- When leaching is compared between cement mortars and concrete with and without coal fly ash, cement mortars and concrete containing fly ash had somewhat higher upper bounds for the

ranges of leached concentrations for barium, cobalt, copper, molybdenum, phosphorus, antimony, silicon (at pH>6) and vanadium (at 4 <pH<8) based on pH dependent leaching tests (with the expected field pH to range from 7 to 13). Based on monolith leaching tests, higher upper ranges of leaching were observed in some cases containing fly ash for boron, cadmium and molybdenum.

- In comparison to Dutch national criteria for leaching from construction materials, only selenium approached or exceeded the limit value for unrestricted use in one case out of seventeen. In addition to selenium, only maximum values for antimony and cadmium were within an order of magnitude of the Dutch regulatory limits.
- USEPA HBNs were exceeded at the mean concentration for pH dependent leaching over the pH domain of 7 to 13 by arsenic, chromium and cobalt. HBNs are exceeded by the 90 percent confidence interval additionally by molybdenum, lead, antimony, selenium, strontium and vanadium. However, the comparison of pH dependent leaching test results to HBNs does not consider reductions in leaching concentrations resulting from the physical form of the material, nor dilution and attenuation from the point of release at the material interface to the point of compliance (e.g., a down-gradient aquifer or drinking water well).
- Leaching of COPCs from fly ash was not increased by incorporation of the fly ash in cement materials, based on comparison between leaching test results of fly ash alone and fly ash in cement materials. This suggests that use of fly ash in concrete will not increase the overall leaching of COPCs from fly ash into the environment.
- Arsenic leaching from fly ash was decreased for several cases by incorporation into cement materials. Also, chromium leaching is decreased when reducing materials (such as ground granulated blast-furnace slag) are used as part of the cement material formulation.
- Using the pH dependent and monolith leaching test data, as described in the LEAF methodology, provides a more robust approach than single extraction leaching tests for evaluating the potential environmental impacts from use of coal fly ash in cement and concrete materials because LEAF considers the likely range of leaching pH over the material's lifecycle and the physical form of the materials (i.e., monolithic or granular). Single extraction leaching tests cannot adequately describe the leaching characteristics of COPCs accounting for the likely environmental pH domain and physical form.

The available data suggest that the use of coal combustion fly ash in cement materials, for different combinations of fly ash source and usage rates, will not increase leaching of some constituents to levels greater than typical ranges for cement materials not containing fly ash. However, there are data limitations that preclude making broad based claims for some usage rates and fly ashes including those resulting from changes in air pollution control at coal-fired power plants. For example, fly ash substitution rates for cement of up to ca. 45 wt% is typical in US large commercial concrete applications, while the predominance of materials reported here have ca. 20-35 wt% fly ash substitution. Based on available data (31 cement mortar and concrete samples containing coal fly ash in comparison to 21 cement and mortar samples that did not contain coal fly ash), results indicate that some (and likely a

large portion) of coal fly ashes can be used in cement and concrete formulations without causing a greater range in leaching of COPCs than observed from analogous cement materials not containing fly ash and without causing adverse environmental impacts. The range of fly ash sources and usage rates for cement materials with pH dependent and monolith leaching test data available is more limited than the full range of typical fly ash usage rates and typical fly ash leaching behavior (i.e., leaching of the fly ash is unknown for most cases evaluated here and fly ash leaching of constituents of potential concern has been demonstrated to vary over up to four orders of magnitude in concentration). In addition, while the data are indicative of expected leaching behavior for fly ashes currently being produced, the data evaluated in this report does not consider changes in leaching from cement-based materials that may occur if the characteristics of coal fly ash used in cement-based materials change in response to recent changes in air pollution control requirements for coal fired power plants. To the extent that such changes affect the fly ash characteristics, the available data sets do not allow evaluation of the impacts of the following potential changes to air pollution controls at coal fired power plants: (i) addition of activated carbon or halogenated activated carbon, (ii) a shift in the coal types burned or blends thereof to achieve new air pollution control limits, (iii) presence or increase in ammonia in the ash because of excess ammonia injected as part of SCR NO<sub>x</sub> controls, and (iv) the inclusion of sorbent from use of dry sorbent injection systems (i.e., trona (sodium sesquicarbonate), sodium carbonate or hydrated lime).

This study should be viewed as the beginning of a collection of robust leaching characterizations for fly ash and fly ash amended cementitious materials, high fly ash replacement materials such as solidification/stabilization formulations, and other utilization applications. It is prudent to develop a characterization and quality control program to determine which combinations of fly ash and cement formulations have leaching characteristics within the typical range for cement materials without fly ash.

Furthermore, without comparison to risk-informed criteria, potential increases in leaching of some COPCs, demonstrated through direct comparisons between materials with and without fly ash, does not indicate that the use of fly ash as a supplemental cementitious material will result in adverse impacts to human health or the environment. Thus, the approach taken in this report should be used to develop an evaluation basis (e.g., thresholds, regulatory guidance structure, and quality control program) for the acceptability of leaching characteristics greater than the typical range for cement-based materials without fly ash. The systematic behavior of COPC leaching from cement materials produced using fly ash will allow determination of the general coal sources and coal combustion facility configurations that result in ash that is acceptable for use at intermediate or high usage rates (i.e., 10-30 wt% or up to 50% of the cement dry mixture), and reduce the extent of needed quality control testing.

## **Table of Contents**

Acknowledgements.....	ii
Abstract.....	iii
Executive Summary.....	iv
Table of Contents.....	viii
List of Figures.....	x
List of Tables.....	x
Acronyms and Abbreviations.....	xi
Introduction.....	1
Approach.....	2
pH-Dependent Leaching Tests.....	3
Single Extraction Leaching Tests.....	4
Data Sources and Materials Evaluated.....	5
European Mortar and Concrete Samples.....	5
US Fly Ash, Mortar and Concrete Samples (CBP).....	6
Cement Admixture Paste Samples.....	6
Concrete Pavement Study (Cheng et al., 2008).....	7
Concrete Prepared with Canadian Fly Ash (Zhang et al., 2001).....	7
Limitations of the Data Sources and Materials Evaluated.....	8
Quality Assurance and Quality Control.....	8
Data Management Using LeachXS™.....	9
Results and Discussion.....	10
Comparison of CEM I and CEM II/B-V Cement Mortars (EU data).....	10
Comparison of CBP Cement Grout, Mortar and Concrete with Fly Ash (US data).....	15
Comparison of Cement Admixture Paste Containing Fly Ash.....	15
Comparison of Studied Fly Ash Samples with Other Fly Ash Characterization.....	16
Comparison of Single Extraction Leaching Test Results (US and Canadian data) with pH Dependence Leaching Test Results and Health Based Numbers.....	16
Conclusions.....	22
References.....	24
Appendices	

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes*

Appendix A. pH Dependent Leaching of EU Cement Mortars: CEM I (without fly ash) and CEM II/B-V (with fly ash) .....	28
Appendix B. Comparisons of Leaching Results and Statistics (i.e., Median and Maximum Values) for pH-Dependent Leaching from Cements and Concretes with and without Fly Ash .....	36
Appendix C. Cumulative Release from Monolith Leaching of EU Cement Mortars and Concretes: CEM I (without fly ash) and CEM II/B-V (with fly ash).....	41
Appendix D. Approach for Criteria Development for Monolithic Materials in the Dutch Soil Quality Decree (2007) .....	52
Appendix E. Effect of Carbonation on Monolith Leaching of EU Cement Mortars: CEM I (without fly ash) and CEM II/B-V (with fly ash).....	55
Appendix F. pH Dependent Leaching of CBP Cement Mortars and Concrete Containing Fly Ash .....	59
Appendix G. Cumulative Release from Monolith Leaching of CBP Cement Mortars Containing Fly Ash.....	63
Appendix H. pH Dependent Leaching of a Fly Ash (CFA2) and a Fly Ash-Containing Cement Mortar (MBD2) .....	67
Appendix I. Cumulative Release from Monolith Leaching of a Fly Ash-Containing Cement Mortar (MBD2) .....	70
Appendix J. pH Dependent Leaching of Fly Ash Samples (FAF and CFA2) Compared to the Range of USEPA Fly Ash Leaching Data .....	74
Appendix K. pH Dependent Leaching of EU CEM II/V-B and Single Extraction Leaching Results (Cheng et al., 2008 and Zhang et al., 2001) Compared to the USEPA Health-based Numbers .....	57

## List of Figures

Figure 1. pH-dependent leaching test results for arsenic, boron, chromium and molybdenum from EU mortar samples of CEM I (Portland-without fly ash; left side graphs) and CEM II/B-V (P+CFA - with fly ash; right side graphs). Dashed lines indicate mean and 90% confidence intervals. A sample legend is provided in Appendix A.....	11
Figure 2. Mass transfer testing results for cumulative release of arsenic, boron, chromium and molybdenum from EU mortar samples of CEM I (Portland-without fly ash; left side graphs) and CEM II/B-V (P+CFA - with fly ash; right side graphs). Grey data represent concretes (vs. mortars) with fly ash replacement. Dashed lines indicate mean and 90% confidence intervals. Horizontal solid line represents the Dutch regulatory criterion for unrestricted use of construction products. A sample legend is provided in Appendix C. ....	12
Figure 3. Annotated graph showing leaching data relative to health based numbers (HBNs) over a relevant pH range for cementitious materials. ....	17
Figure 4. Statistical representation (mean with 90% confidence limits) of concentrations of the EU CEM II/V-B cement mortars and concretes containing fly ash and literature single extraction test results (Cheng et al., 2008; Zhang et al., 2001) compared to health based numbers (HBNs) over a relevant pH range of 7 to 13.....	19
Figure 5. Statistical representation (mean with 90% confidence limits) of concentrations of the EU CEM II/V-B cement mortars and concretes containing fly ash and literature single extraction test results (Cheng et al., 2008; Zhang et al., 2001) compared to health based numbers (HBNs) over a relevant pH range of 7 to 13.....	20

## List of Tables

Table 1. Component Compositions for CBP Mortars and Concrete samples. ....	6
Table 2. Component Compositions for Concrete Pavements (Cheng et al., 2008). ....	7
Table 3. Component Compositions for Concrete Samples (Zhang et al., 2001). ....	8
Table 4. Comparison of Release from CEM I and CEM IIB Mortars and Concretes with Dutch Regulatory Criteria. ....	14
Table 5. Comparisons of the ratio of the maximum value of the 90 percent confidence interval to the HBN (Max/HBN) and the maximum value of the mean values to the HBN (Mean/HBN).....	21
Table C-1 Maximum permissible addition value for soil (MPA <sub>s</sub> ) and groundwater (MPA <sub>g</sub> ) used in the derivation of emission limits for granular construction products in the Dutch Soil Quality Decree.....	52

## **Acronyms and Abbreviations**

BGM	backfill grout mortar
BMD	Building Materials Decree (Dutch regulation)
CBP	Cementitious Barriers Partnership
CCR(s)	coal combustion residue(s)
CEN	Comité Européen de Normalisation (European Standardization Committee; <a href="http://www.cen.eu">http://www.cen.eu</a> )
COPC(s)	constituent of potential concern
EU	European Union
HBN	health based numbers (USEPA)
L/A	liquid-to-surface area ratio
LEAF	Leaching Environmental Assessment Framework
L/S	liquid-to-solid ratio
LSP	liquid-solid partitioning
MBD2	material blank in deionized water (second of two materials)
MPA	maximum permissible addition (Dutch SQD criteria)
MPC	maximum permissible concentration (Dutch SQD criteria)
NEN	Nederlands Normalisatie Instituut (Dutch Standardization Institute)
RvA	Raad voor Accreditatie (Dutch Accreditation Council; <a href="http://www.rva.nl">http://www.rva.nl</a> )
SCM(s)	supplemental cementitious material(s)
SPLP	Synthetic Precipitation Leaching Procedure (USEPA, SW-846 Method 1312)
SQD	Soil Quality Decree (revision to Dutch BMD)
S/S	solidification/stabilization
SVC	structural vault concrete analogous mortar
TCLP	Toxicity Characteristic Leaching Procedure (USEPA, SW-846 Method 1311)
VCT	vault concrete
USDOE	United States Department of Energy
USEPA	United States Environmental Protection Agency

## **Introduction**

The potential environmental impacts of disposal and beneficial use of coal combustion residues (CCRs) have recently come under increased scrutiny. The United States Environmental Protection Agency (USEPA) has proposed alternatives for regulating management of coal fly ash (75 Federal Register 35127). In 2010, 26 of the 68 million tons of coal combustion fly ash produced in the US were used in commercial applications (ACAA, 2012). Approximately 11 million short tons were used as supplemental cementitious materials (SCMs), replacing a portion of portland cement powder used in concrete, concrete products and grout. Other large volume uses of coal fly ash in the US include use as raw feed for cement production (2.0 million tons), placement in structural fill and embankments (4.7 million tons), various mining applications (2.4 million tons), and as a matrix component in waste solidification/stabilization (3.3 million tons). These uses are considered beneficial because addition of fly ash to cement-based materials (i) improves the physical and durability characteristics, (ii) conserves landfill space by utilizing otherwise disposed materials, and (iii) reduces the need for and environmental impacts associated with processing new raw materials. However, default use of CCRs as SCMs without the consideration of resulting environmental impact potentially may lead to adverse impacts to soil or groundwater and surface waters. Thus, in the case of CCRs used within the cement industry, there is a need for evaluation of both the potential environmental impacts from use of coal fly ash in cement and cement products, as well as potential impacts from disruption to the availability of coal fly ash for commercial use in these materials. Leaching is considered a primary pathway for environmental impact of cement products containing coal fly ash through the release of constituents of potential concern (COPCs) to soils and runoff that can impact surface water or groundwater.

The objective of this report is to compare the leaching of portland cement-based materials that have been prepared with and without coal combustion fly ash to illustrate whether there is evidence that the use of fly ash in cement and concrete products may result in increased leaching of COPCs compared to cement and concrete products that do not contain fly ash. A subsidiary objective is to determine if there is evidence that incorporation into cement materials increases the leaching of COPCs from fly ash, thereby potentially increasing COPC release from fly ash through the use in cement and concrete. The following types of comparisons are made in the report:

- The range of leaching performance for cement mortars from the European Union (EU) formulated without fly ash is compared to EU cement mortars and concretes formulated with fly ash as a primary constituent. In this comparison, the leaching characteristics and specific origin (e.g., coal source, facility configuration, and handling processes) of the fly ash materials are not known although the fly ash was required to meet specifications according to EU standard EN 197-1.<sup>1</sup> Test data are compared with Dutch regulatory criteria for construction products in service life.

---

<sup>1</sup> EN 197-1 specifies physical properties of suitable fly ash and major chemical constituents (i.e., calcium, silica, iron) but does not contain specifications regarding constituents of potential concern from an environmental perspective.

- The range of leaching performance for a series of US cement mortar samples with different amounts of fly ash, taken from the Cementitious Barriers Partnership (CBP),<sup>2</sup> is compared to leaching from samples of the component fly ash material used in the mortar formulations. In addition, the 90 percent confidence intervals with respect to leaching from the EU cement mortars containing fly ash are included in this comparison to place the results into context with the EU dataset.
- Leaching performance of a blended cementitious paste representative of solidification/stabilization (S/S) formulation and the fly ash used in that paste. The 90 percent confidence intervals from EU cement mortars with fly ash substitution are included to place these materials in context to the EU dataset.
- Leaching evaluation using single extraction leaching tests in comparison to results from multi-extraction pH dependence granular batch testing and monolith testing. Single extraction and pH dependence leaching test results are also compared to USEPA health based numbers (HBNs).

This report evaluates the results obtained from studies carried out for other purposes in a new context, and as such the observations and conclusions of this report should be considered indicative of performance but not inclusive or necessarily representative of the full range of possible coal fly ashes used in cement and concrete or leaching performance of the resulting materials.

## **Approach**

Traditionally, the results of one or more leaching tests have been used to estimate the leaching potential of waste or other materials in situations where the material is placed in a landfill or used on the land. The goal of leach testing has been to assess potential contaminant release and the likelihood of soil, surface water or groundwater contamination resulting from specific management scenarios for wastes and other materials. The current regulatory leaching tests in the US are single-batch extraction procedures designed to simulate leaching under conditions considered to represent a plausible “mismanagement” scenario for a hazardous waste disposed in a municipal waste landfill. These tests were not specifically designed to address potential beneficial use applications such as fly ash use in cements and concretes.

The Leaching Environmental Assessment Framework (LEAF) is an environmental assessment methodology consisting of a set of leaching test methods, scenario-based leaching assessment models, and information management tools designed to provide more robust estimates of constituent leaching under a wider range of potential field conditions than current approaches based on single-extraction tests. The methodology for leaching assessment using LEAF is based on a tiered testing approach (Kosson et al., 2002). As opposed to the scenario simulation tests currently in wide use, the LEAF leaching methods are intended to generate characteristic leaching behavior data for a material over a

---

<sup>2</sup> The Cementitious Barrier Partnership is a research program supported by the Office of Environmental Management at the US Department of Energy. The project is aimed at improving the prediction of performance of cementitious materials used in nuclear processing and waste management applications (see [www.CementBarriers.org](http://www.CementBarriers.org) for more information and reports prepared under this program).

broad range of test conditions designed to encompass the range of plausible conditions for actual management. The resulting data can be applied to assess leaching potential under anticipated field conditions for one or more management scenarios. For evaluation of cements and concretes containing fly ash, batch pH dependence and monolith mass transfer leaching tests are the most appropriate because they account for range of potential leaching pH during the material's lifecycle and the physical form of the material. The LEAF approach has been developed in close coordination with EU efforts to adopt a similar set of test methods in Europe through the European Standardization Committee (Comité Européen de Normalisation; CEN).

Several research studies have used the LEAF test methods or the European counterparts to characterize leaching from portland cement-based materials and from the components used in the material formulation. Within these studies, the primary fundamental leaching characteristics for cement-based materials have been (i) leaching as a function of pH as the result of Method 1313, CEN/TS 14429 or CEN/TS 14497 and (ii) monolithic mass-transfer rate leaching using Method 1315, NEN 7345, CEN/TC 351 TS-2 or CEN/TS 15863, often referred to as "diffusion testing" or "tank leaching tests." In all cases, eluates produced from the leaching tests were analyzed by inductively coupled plasma optical emission spectroscopy or inductively coupled plasma mass spectroscopy to measure concentrations of leached constituents. These leached concentrations, or derived measurements such as cumulative release, are then used in the data analysis presented in this report. In addition, test results from two studies using single point leaching tests (i.e., the Synthetic Precipitation Leaching Procedure (SPLP, USEPA Method 1312) and deionized water leaching (ASTM D3987-85) are compared to results from the multipoint pH dependence leaching tests.

### pH-Dependent Leaching Tests

Method 1313 is an equilibrium-based leaching test designed to provide aqueous extracts representing the liquid-solid partitioning (LSP) curve of constituents as a function of eluate pH value. This procedure consists of nine parallel batch extractions at targeted pH values and one extraction at the natural pH<sup>3</sup> of the material. The solid material may require particle size reduction by crushing in order to facilitate the approach to solid-liquid equilibrium within a reasonable extraction timeframe. Dilute acid or base in deionized water is added to each extraction according to a pre-test titration in order to achieve final extract pH values at specified target values ranging between 2 and 13 at a liquid-to-solid ratio (L/S) of 10 mL/g-dry after 24 hours<sup>4</sup>. The pH and conductivity of the final extract solution are recorded and vacuum- or pressure-assisted filtration is used to separate the liquid and solid phases prior to chemical analysis of the eluate. Eluate concentrations for constituents of interest are plotted as a function of eluate pH allowing for comparison to quality control and assessment limits.

The European pH-dependence methods, CEN/TS 14429 (2005) and CEN/TS 14497 (2005), are similar to Method 1313 in both test structure and intent with directly comparable results (Garrabrants et al.,

---

<sup>3</sup> The natural pH (also referred to as "own pH") is the final eluate pH response of a deionized water extraction of a solid material (i.e., no acid or base added) conducted at an L/S 10 mL/g-dry.

<sup>4</sup> 24 hours is the specified extract time for materials size reduced to a particle size of less than 300 µm. Longer extraction times are specified for larger particles.

2012a). In the CEN methods, separate sample portions are extracted in parallel in dilute acid or base solutions in order to reach stationary pH values at the end of the extraction period at a fixed L/S of 10 mL/g. At least eight final pH values are required, covering at a minimum the range from pH 4 to pH 12 (including the lowest value  $\text{pH} \leq 4$  and the highest value  $\text{pH} \geq 12$ ). The maximum pH differential between final pH points shall not exceed 1.5 pH units. The primary difference between these two methods is how the extraction solution is introduced to the test portion. For CEN/TS 14429, sample portions are contacted with extraction solutions in a closed vessel with acid/base introduction through initial addition of extraction fluid. At the start of the test, the extraction solutions are prepared and divided evenly into three fractions. A fraction of extraction solution is added to the extraction bottle at the start of the test, after 30 minutes, and after 2 hours. For CEN/TS 14497, sample portions are placed into a partially open vessel with reagent water and acid or base is introduced via automated pH control.

#### Monolithic Mass Transfer Rate Leaching Tests

Method 1315 involves leaching of a continuously water-saturated monolithic or compacted granular material in a water-filled tank with periodic renewal of the leaching solution. The vessel and sample dimensions are chosen so that the sample is fully immersed in the leaching solution. Samples are contacted with reagent water at a liquid-to-surface area ratio (L/A) of  $9 \pm 1 \text{ mL/cm}^2$  sample surface area. The leaching solution is exchanged with fresh reagent water at nine pre-determined intervals over a cumulative period of 63 days. For the CBP samples, leaching with periodic leachant renewals was extended to a cumulative period of 231 days. The eluate pH and specific conductance is measured for each time interval and analytical samples are collected and preserved based on the determinative methods to be performed. These data are used to estimate release rate and mass transfer parameters (i.e., observed diffusivity) for each constituent of interest. For the comparative purposes of this report, cumulative release as a function of time is plotted for each constituent of interest.

Determination of constituent release and mass transfer rates from monolithic materials was performed according to NEN 7345 (1994), CEN/TC 351 TS-2 (2009) or CEN/TS 15863 (2009) for EU mortar and concrete samples. These methods are very similar in approach and operation to Method 1315. The differences between the test methods include minor differences in details, such as the specified L/A ratio, the number of leaching cycles and the times of leachant renewal, which are not considered critical for determining rates of cumulative release (Garrabrants et al., 2012b).

#### Single Extraction Leaching Tests

SPLP (USEPA SW-846 Method 1312; USEPA 1992b) is a single batch extraction carried out with synthetic acidic precipitation at a liquid/solid ratio of 20 mL/g and a contacting extraction period of  $18 \pm 2$  hours. Testing carried out by Cheng et al (2008) used SPLP Extraction Fluid 1 which is specified as a 60/40 weight percent mixture of sulfuric and nitric acids added to reagent water to attain a pH of  $4.20 \pm 0.05$ . The pH of the resulting eluate is measured at the time of eluate filtering and influenced by the composition of the material extracted. For cementitious materials, the eluate pH is expected to be alkaline. ASTM International D3897-85 (ASTM 1990), also used by Cheng et al (2008), is similar to SPLP but is carried out using deionized water as the extraction fluid.

Zang et al (2001) carried out single batch extractions of 10.2 cm diameter by 2.0 cm thick disks cut from portland cement cylinders (see following section). Each disk was submerged in a synthetic acid precipitation prepared similarly to the SPLP Extraction Fluid 1 but adjusted to a pH of 4.5. Each sample was submerged in the extraction fluid at a liquid to solid ratio of 5 mL/g for up twenty-four weeks. The extraction fluid was sub-sampled and analyzed at 6 time periods, with results reported for extractions after 20 weeks of contact for cadmium, chromium, copper, iron, nickel, lead, selenium and zinc. Results from extraction after 24 weeks of contact were reported for arsenic.

Results from the above studies that used the Toxicity Characteristic Leaching Procedure (TCLP; USEPA SW-846 Method 1311; USEPA, 2012a) or other extractions with acetic acid under different conditions were not included in this evaluation because (i) acetic acid is used to mimic co-disposal with municipal solid waste, which is not the management scenario being considered here, and (ii) acetic acid can result in complexation and therefore increased concentrations of some COPCs (i.e., lead) in resulting extracts which is not considered relevant.

### Data Sources and Materials Evaluated

#### *European Mortar and Concrete Samples*

A series of standard mortar samples, prepared using Type I (CEM I) portland cements according to the European cement standard EN 197-1 manufactured predominately at several European facilities, were characterized using pH-dependent leaching tests (CEN/TS 14429 or CEN/TS 14497) and mass transfer leaching tests (CEN/TC 351 TS-2 or CEN/TS 15863). Standard mortar samples were prepared using 22 wt% cement, 68 wt% sand and 11 wt% water (water-to-binder ratio of 0.50) in accordance with the European standard EN 196-1 (2005). Mortar samples for leaching evaluation were removed from molds after curing for 24 hours and cured at 20 °C and 95% relative humidity for an additional 27 days in plastic bags. The comparison set of mortars which include fly ash were prepared in a similar manner using CEM II/B-V cements, which are blended cements containing 21-35% fly ash substituted for cement powder (van der Sloot, 2000; van der Sloot et al., 2001a; van der Sloot et al., 2008a).

In order to illustrate the range of cumulative release for constituents in concretes as well as the above cement mortars, leaching test data for concrete 15-cm cubic samples from Dutch national studies also have been included in the evaluation of the EU CEM II/B-V mortar samples.<sup>5</sup> Test results were taken from studies evaluating fly ash replacement in mortar and concrete using worldwide sub-bituminous coal sources in the range of 10-30% replacement (van der Sloot et al., 1985; van der Sloot and Weijers, 1987). In addition, test results on uncarbonated and carbonated mortars (with and without fly ash) were taken from a study evaluating the effect of carbonation of concrete samples with 20% cement replacement by coal fly ash on leaching conducted for a Dutch cement producer (ECN, 2000). The effects of carbonation are considered relevant because carbonation through reaction of alkali in cement with atmospheric carbon dioxide is a primary aging mechanism for cementitious materials that can

---

<sup>5</sup> Often, mortars are used instead of concrete to assess leaching during laboratory testing. This approach assumes that the coarse aggregate present in the concrete but not used in the mortar is chemically inert. However, no studies have been identified that provide a direct comparison of the leaching performance for mortars and concretes that have the same formulation except for the presence of the coarse aggregate.

change both the chemical (i.e., decreasing pH and changing chemical speciation) and physical properties (i.e., change in porosity and pore structure) of the material.

*US Fly Ash, Mortar and Concrete Samples (CBP)*

Leaching behaviors of three cementitious reference mortars containing a well-characterized fly ash (sample FAF) have been studied as part of the Cementitious Barriers Partnership (Arnold et al., 2011). The mortar formulations include a flowable stable (zero-bleed) infill/backfill grout (material code BGM), a structural vault concrete-analogous mortar (material code SVC), and a vault concrete (material code VCT). The binders used in these materials include ternary blends (Type I/II cement, blast furnace slag and Class F fly ash) for BGM and SVC and a quaternary blend (Type V sulfate-resistant cement, blast furnace slag, Class F fly ash binder, silica fume) for VCT. Formulations for each of the sample types are provided in Table 1.

In addition to characterization of the blended materials, leaching tests were performed on the component source materials including ground granulated blast furnace slag, coal combustion fly ash (material code FAF), quartz concrete sand, and Type I/II portland cement powder.

**Table 1. Component Compositions for CBP Mortars and Concrete samples.**

Component	BGM (wt%)	SVC (wt%)	VCT (wt%)
Type I/II Cement (ASTM C 150)	5.9	5.4	-
Type V Cement	-	-	5.5
Grade 100 Blast Furnace Slag (ASTM C 989)	13.5	8.0	7.3
Type F Fly Ash (ASTM C 618)	6.6	16.9	4.3
Silica Fume	-	-	1.2
Water (maximum)	11.8	14.6	6.9
Quartz Sand (ASTM C 33)	62.3	55.0	24.7
No. 67 Granite Aggregate (ASTM C 33)	-	-	50.1
Fly ash in cementitious dry mixture	25.3	55.8	23.5

Notes:

- BGM = backfill grout mortar
- SVC = structure vault concrete analogous mortar
- VCT = vault concrete

*Cement Admixture Paste Samples*

A study of solidification/stabilization (S/S) of a reference waste stream from nuclear waste treatment was carried out which included leaching characterization of a fly ash (sample CFA2) and a matrix blank (sample MBD2) consisting of a Portland cement paste containing the same fly ash (Garrabrants et al., 2008). The MBD2 consists of a tertiary binder of fly ash, steel slag and Portland cement with a final water-to-binder ratio of 0.4, resulting in a final composition of 28 wt% fly ash, 28 wt% slag, 5 wt%

cement and 40 wt% water (45.9 wt% fly ash in the cementitious dry mixture). The MBD2 samples were cured at least 30 days in sealed containers prior to leach testing. Characterization included pH-dependent leaching and monolith leaching according to methods SR02.1 and MT01, respectively, which are predecessors to Method 1313 and Method 1315 (Kosson et al., 2002). In this study, a cement mix not containing fly ash was not characterized separately, so the only comparison that can be made is between fly ash leaching and the leaching of the cementitious material containing the same fly ash.

*Concrete Pavement Study (Cheng et al., 2008)*

Cheng et al. (2008) carried out a study examining the leaching of simulated concrete pavements prepared with and without coal fly ash. A Class F fly ash obtained from a power plant located in Ohio (US) was used in the concrete preparation at 0, 30 and 50 wt% of the dry cement material mixture (Table 2). Samples of each concrete mix were cured for four weeks prior to leaching evaluation using SPLP and ASTM D3897 (deionized water extraction). However, separate leaching analysis of the fly ash using either test was not reported. Runoff samples were also collected from the simulated pavement after intervals of cyclic loading intended to simulate traffic on the pavement.

**Table 2. Component Compositions for Concrete Pavements (Cheng et al., 2008).**

Component	PC (wt%)	PC30 (wt%)	PC50 (wt%)
Type I/II Cement	16.2	11.4	8.1
Type F Fly Ash (ASTM C 618)	-	4.8	8.1
Water (maximum)	6.0	6.0	6.0
Sand	31.2	31.2	31.2
No. 57 Aggregate	46.6	46.6	46.6
Fly ash in cementitious dry mixture	-	30	50

*Concrete Prepared with Canadian Fly Ash (Zhang et al., 2001)*

Zhang et al (2001) carried out a study examining the leaching of concrete samples prepared using ASTM Class F coal fly ash obtained from two Canadian sources: Lingan, Nova Scotia (burning bituminous coal) and Forestburg, Alberta (burning sub-bituminous coal). Concrete samples were prepared using Lingan fly ash as 30 and 60 wt% of the dry cement material mixture and with Forestburg fly ash as 30 wt% of the dry cement material mixture (Table 3). Multiple water-to-cement (w/c) ratios were used in the concrete mixes. A control concrete that did not contain fly ash also was evaluated. Concrete mixes were cured for 28 days prior to leaching evaluation using concrete disks submerged in synthetic acid precipitation for up to 24 weeks as described earlier.

**Table 3. Component Compositions for Concrete Samples (Zhang et al., 2001).**

Component	Sample	T0 (wt%)	T2 (wt%)	T5 (wt%)	T14 (wt%)	T15 (wt%)	T17 (wt%)
Type I Cement		13.6	9.7	9.9	5.6	12.1	6.9
Fly Ash		0.0	4.2	4.2	8.3	5.2	3.0
Water		6.8	6.9	7.1	7.0	6.9	6.9
Sand		31.7	31.5	31.4	31.7	30.3	33.2
Coarse Aggregate		47.9	47.7	47.5	47.5	45.5	49.9
Fly ash in cementitious dry mixture		0	30	30	60	30	30
Fly ash source		-	Lingan	Forestburg	Lingan	Lingan	Lingan
Water/(cement+fly ash) ratio		0.5	0.5	0.5	0.5	0.4	0.7

### Limitations of the Data Sources and Materials Evaluated

The following are key limitations of the data sources and materials evaluated in this report:

- The EU mortar and concrete samples were prepared using pre-packaged blended cement formulations, and therefore the source and leaching characteristics of the fly ash used in these materials are unknown. Thus, it is unknown whether the fly ash materials used had high, medium or low leaching with respect to COPCs. However, fly ash used in CEM II/B-V cements must conform to EU standard EN 197-1, which specifies physical properties, loss on ignition, chloride content and reactive calcium content but does not consider constituents typically of environmental concern.
- The US mortar and concrete samples (CBP samples and MBD2) were prepared with additional admixtures, including reducing materials (e.g., blast furnace slag or steel slag) which can impact the leaching chemistry for several constituents.
- The studies by Cheng et al. (2008) and Zhang et al. (2001) did not include relevant separate leaching characterization of the fly ash and only limited (e.g., single point) leaching of the resulting cement and concrete materials.
- None of the studies examined included a representative comparison of (i) the range of fly ash types with COPC leaching that typifies the ranges of leaching observed for US fly ash sources, (ii) the effect of fly ash loading up to typical high loading rates in US commercial concretes (e.g., ca. 45 wt% fly ash substitution for cement), including comparison using the same components without fly ash, (iii) the effect of material aging, including extended cure times and carbonation, on COPC leaching, (iv) the impact of using mortar samples as surrogates for testing concrete.

### Quality Assurance and Quality Control

Two laboratories, Vanderbilt University (VU) and The Energy Research Centre of The Netherlands (ECN) were responsible for the leaching characterization of fly ash, cement mortars and concrete discussed in this report. VU carried out the leaching characterization of CBP fly ash, mortar and concrete samples, as

well as the cement admixture paste sample (MBD2) as part of research on behalf of the Department of Energy, Office of Environmental Management. At VU, leaching procedures and chemical analyses were carried out under the same quality assurance and quality control procedures specified in the Quality Assurance Project Plan for characterization of coal combustion residues for research carried out on behalf of USEPA (USEPA, 2011).

ECN carried out all leaching characterization of European cement and concrete samples included in this report. ECN has for more than two decades been a national and international leader in developing and carrying out leaching characterization methods. Since 1983, ECN has been actively involved in the development of leaching tests in support of national (The Netherlands) and European legislation (European Landfill Directive, 2002; Requirement 3 on Health and Environment in the Construction Products Directive, 1989; End of Waste Directive; in development) through chairmanship of working groups in the national standardisation body (Nederlands Normalisatie Instituut, NEN) and the European standardisation organisation CEN. ECN is a qualified laboratory for chemical analysis and for leaching tests under the quality assurance program RvA (Raad voor de Accreditatie) with annual external independent audits on the basis of NEN-EN-ISO 17025. ECN operates under ISO 9000 practice. ECN has participated in many interlaboratory comparison (round-robin) studies for leaching characterization methods which has demonstrated its proficiency (van der Sloot et al., 1994, 1995, 2001b; Hohberg et al., 2000; de Groot et al., 1996). ECN also participated in a recently completed interlaboratory comparison study for *Method 1313: Liquid-Solid Partitioning as a Function of Eluate pH using a Parallel Batch Extraction Procedure* that demonstrated ECN's proficiency in leaching characterization as well as the comparability of results between USEPA Method 1313 and the European pH-dependence methods, CEN/TS 14429 and CEN/TS 14497 (Garrabrants et al., 2011).

Specific quality assurance and quality control programs were not reported for Cheng et al (2008) or Zhang et al. (2001).

#### Data Management Using LeachXS™

Comparisons of leaching test results and statistical representations of leaching behavior were managed using LeachXS™<sup>6</sup>, a program designed specifically to facilitate data management, visualization, and modeling for the large volume of data resulting from robust leaching characterization (van der Sloot et al., 2008b). From the previous studies, the leaching data had been stored in materials databases within LeachXS. Materials were combined into a single materials database, allowing for statistical calculations and comparisons of leaching data. LeachXS contains graphic and report facilitation tools allowing for all comparisons to be output as graphs into Microsoft® Excel spreadsheets.

---

<sup>6</sup> LeachXS is the full-feature version of LeachXS Lite used in recent EPA fly ash characterization research (Kosson et al., 2009) for data management and visualization developed by ECN, Vanderbilt University and DHI (Denmark). The Lite version is freely available for download (free license registration required) at <http://vanderbilt.edu/leaching/downloads/leachxs-lite>.

## **Results and Discussion**

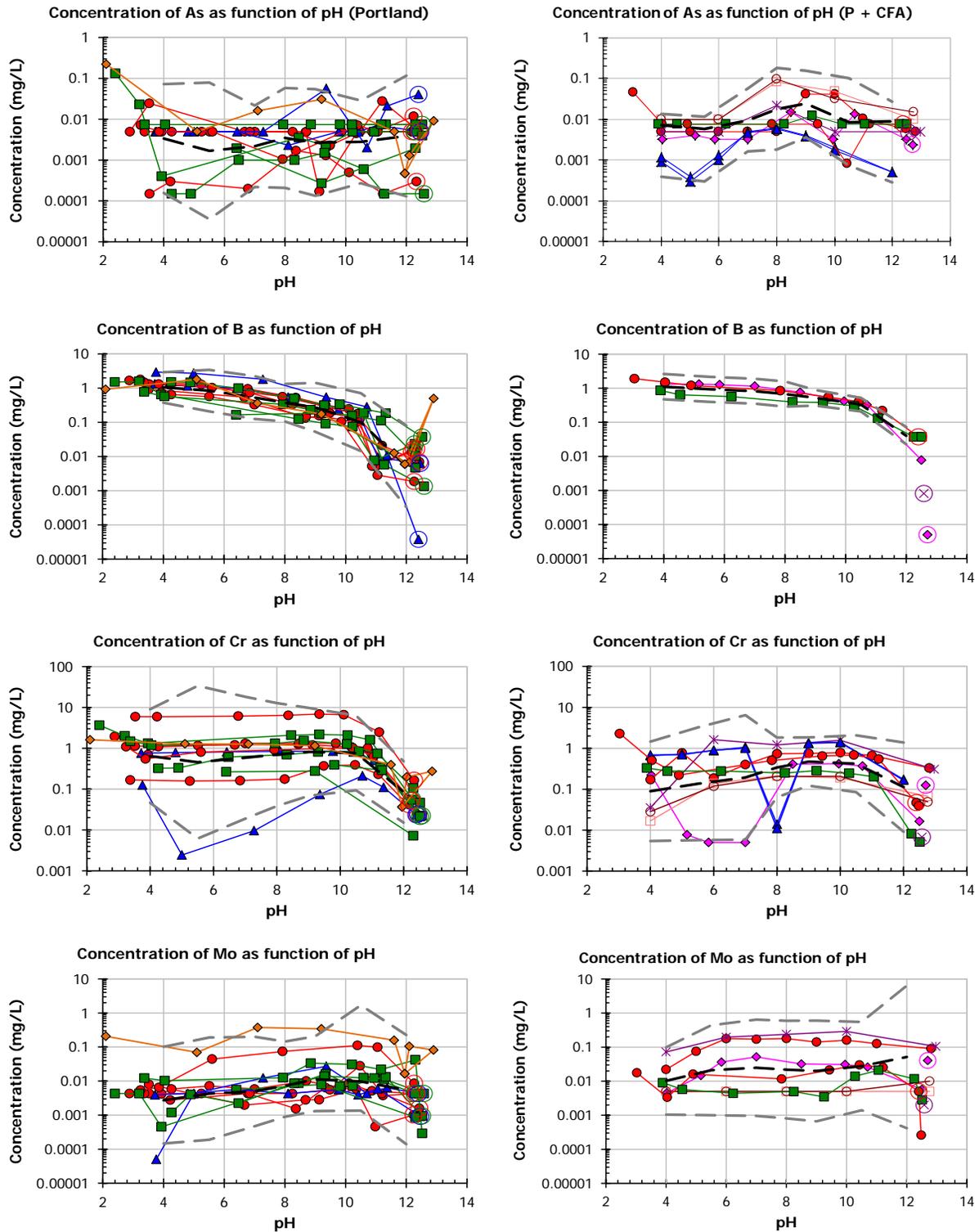
In summary, the cement mortar and concrete data sets evaluated include the following:

- pH dependence leaching test (CEN/TS 14429 or CEN/TS 14997) results for 13 cement mortar and concrete samples without fly ash in the EU data set, including one sample from Thailand, compared with 11 cement mortar and concrete samples prepared with fly ash, including one sample from Brazil and Chile. The specific sources and leaching characteristics of the fly ash used are unknown.
- Monolith mass transfer leaching test results (CEN/TC 351 TS-2 or CEN/TS 15863) for 21 cement mortar and concrete samples without fly ash in the EU data set, including one sample from Thailand, compared with 27 cement mortar and concrete samples prepared with fly ash. The specific sources and leaching characteristics of the fly ash used are unknown.
- pH dependence leaching test (Method 1313) and mass transfer leaching test results (Method 1315) for four cement mortar and concrete samples containing fly ash. The sources and leaching characteristics of the fly ashes (two types) used are known.
- Single extraction leaching test results (either synthetic acid precipitation or deionized water batch extraction) for one fly ash used at three rates (0 -control, 30 and 50 wt% substitution for portland cement) and two additional fly ash samples at three usage rates (0 - control, 30 and 60 wt%). The sources of the fly ash are known but the fly ash leaching characteristics under relevant conditions are not known.

### Comparison of CEM I and CEM II/B-V Cement Mortars (EU data)

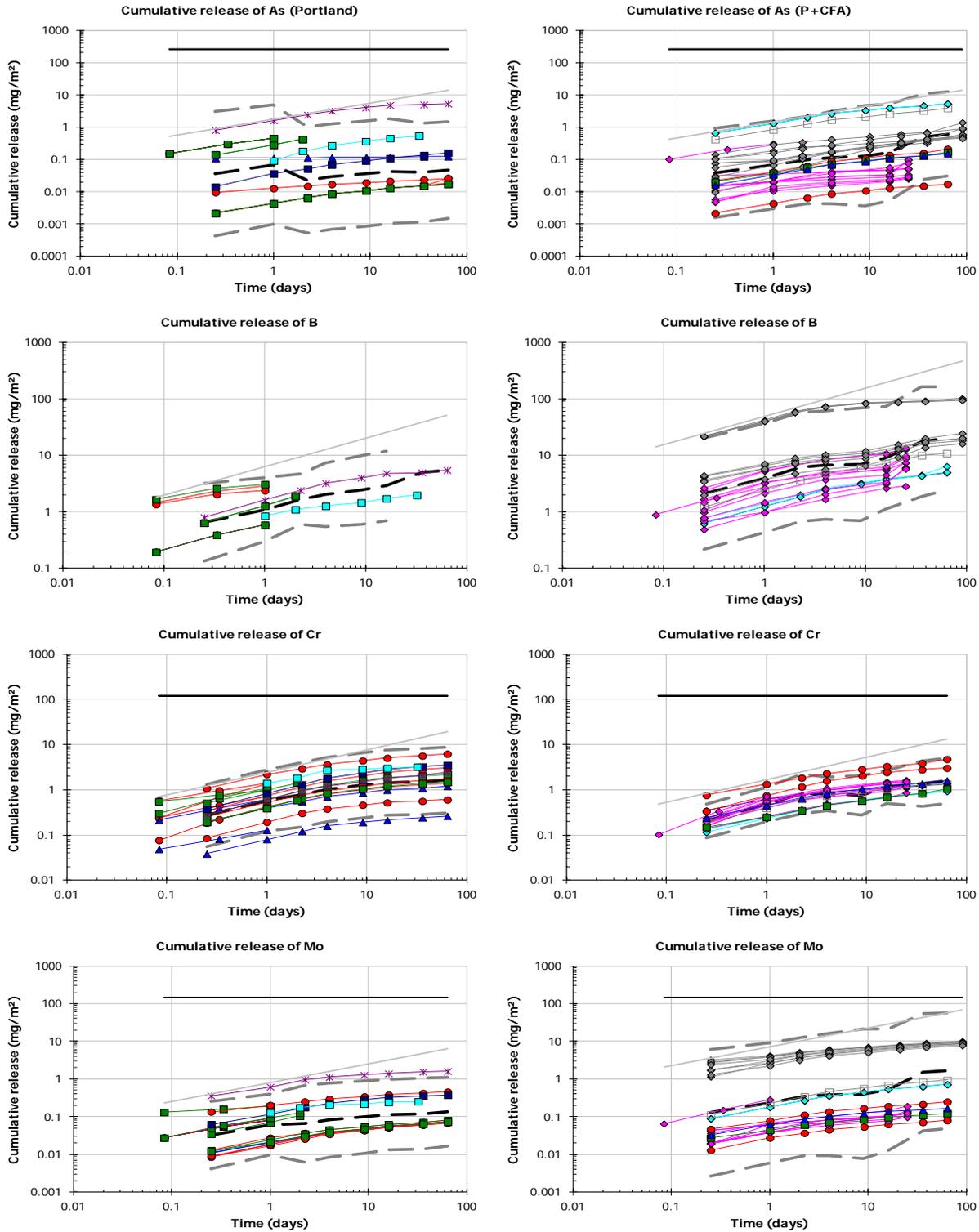
Figures 1 and 2 provide comparisons of leaching from CEM I and CEM II/B-V standard mortars for arsenic, boron, chromium and molybdenum based on pH dependent leaching and monolith leaching, respectively. Complete results of the analyzed constituents from leaching tests are provided for (i) pH-dependent leaching in Appendix A with further comparative analysis on a percentile bases in Appendix B and (ii) monolith leaching in Appendix C. For the pH-dependent data, each of the constituents has a characteristic response of leaching concentration as a function of pH, which is similar for both the cement materials without and with fly ash. From previous studies (Kosson et al., 2009), it is known that fly ash from different sources exhibit several different characteristic leaching concentration as a function of pH responses for each constituent. Thus, cement chemistry appears to control the overall leaching of COPCs from the concrete and mortar materials.

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes*



**Figure 1. pH-dependent leaching test results for arsenic, boron, chromium and molybdenum from EU mortar samples of CEM I (portland-without fly ash; left side graphs) and CEM II/B-V (P+CFA - with fly ash; right side graphs). Dashed lines indicate mean and 90% confidence intervals. A sample legend is provided in Appendix A.**

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes*



**Figure 2.** Mass transfer testing results for cumulative release of arsenic, boron, chromium and molybdenum from EU mortar samples of CEM I (portland-without fly ash; left side graphs) and CEM II/B-V (P+CFA - with fly ash; right side graphs). Grey data represent concretes (vs. mortars) with fly ash replacement. Dashed lines indicate mean and 90% confidence intervals. Horizontal solid line represents the Dutch regulatory criterion for unrestricted use of construction products. A sample legend is provided in Appendix C.

Based on pH dependent leaching test results, there does not appear to be a significant difference in leaching between the cements with or without fly ash replacement for several constituents including: aluminum, arsenic, boron, cadmium, potassium, magnesium, manganese, molybdenum, nickel, lead, sulfur, selenium and zinc. Differences between the cases were considered significant if the upper or lower bounds of the ranges differed by more than approximately one half an order of magnitude. Somewhat higher upper bounds for the ranges of leached concentrations from CEM II/B-V mortars (cement with fly ash replacement) are indicated for barium, cobalt, copper, phosphorus, antimony, silica (at  $\text{pH} > 6$ ) and vanadium (at  $4 < \text{pH} < 8$ )<sup>7</sup>. For all cases, however, there is an insufficient data set to conclude that elevated leaching is statistically significant. Rather, these observations suggest that some ash sources (i.e., fly ashes with high concentrations of leachable constituents of potential environmental concern) when used in concrete and other cementitious materials may result in increased leaching of some constituents from the product material. Calcium leaching has a wider range for CEM II/B-V cement mortars, perhaps resulting from the varied calcium reactivity and concentration in fly ash from different sources.

Analysis of monolith leaching test eluates indicated greater range and greater cumulative release from fly ash amended cement mortars (CEM II/B-V mortars) in some cases for boron, cadmium and molybdenum. Maximum chromium release was slightly lower for cases with fly ash replacement than for cases without fly ash. Cumulative release for the remaining constituents appeared similar for both cement mortar types, without and with fly ash. Concrete samples produced using fly ash containing cement (gray symbols) showed increased cumulative release of arsenic, antimony, boron and molybdenum relative to the corresponding CEM II/B-V cement mortars. While it is unlikely that the presence of the coarse aggregate in the concrete samples resulted in a chemical change relative to the mortar samples, the presence of the coarse aggregate may result in an important change in the physical structure (i.e., pore structure) of the cement paste, as well as the ratio of cement paste to aggregate surface area within the concrete. This observation indicates the need for further research comparing the leachability of concrete in comparison to corresponding mortars.

A comparison is made between the cumulative release up to 64 days as obtained in NEN 7345 (i.e., a monolith leaching test very similar to CEN/TS 15863 and Method 1315) and the regulatory criteria for construction products as defined in the Dutch Soil Quality Decree (SQD, 2007), which follows after the Building Materials Decree (1995)<sup>8</sup>. In Table 4, the maximum release (expressed in  $\text{mg}/\text{m}^2$  at 64 days) for both portland cement mortar and mortar containing coal fly ash is given in comparison with the regulatory limit values (at 64 days) of the SQD for unrestricted use. The Dutch standards were developed considering maintaining soil quality, surface and groundwater quality and protection of human health (see Appendix D for a summary). Relevant or equivalent standards tied to cumulative release from diffusion testing do not exist in the US.

---

<sup>7</sup> Apparent differences in the leaching of iron between the cements with and without fly ash are most likely the impact of different detection limits used in the individual studies. This observation is made considering the constant values of iron concentration at alkaline pH values, which is typical of a non-detected value graphed at the detection limit and is also consistent with known iron chemistry.

<sup>8</sup> This was the first national environmental regulation for construction materials based on leaching assessment.

**Table 4. Comparison of Release from CEM I and CEM IIB Mortars and Concretes with Dutch Regulatory Criteria.**

Analyte	Symbol	Limit value Dutch SQD (mg/m <sup>2</sup> )	Max value* CEM I (mg/m <sup>2</sup> )	Max value CEM II/B V (mg/m <sup>2</sup> )
Arsenic	As	260	0.76	3.8
Barium	Ba	1500	77	168
Cadmium	Cd	3.8	0.08	0.48
Chromium	Cr	120	6.2	4.4
Copper	Cu	98	3.7	3.5
Molybdenum	Mo	144	0.35	7.9
Nickel	Ni	81	2	3.8
Lead	Pb	400	20	11.3
Antimony	Sb	8.7	1.1	4.9
Selenium	Se	4.8	1.6	6.2
Vanadium	V	320	45	5.5
Zinc	Zn	800	3.8	8.6

\*The Max value is the maximum in cumulative release up to 64 days observed from leaching tests carried out on samples as described in this report.

The comparison between cumulative release and the SQD limit values indicate that in most cases the increase in release due to inclusion of fly ash in cement mortar may not be important as the release remains well-below Dutch regulatory criteria derived from an impact assessment to soil and groundwater. However, in the case of cadmium and antimony, maximum leaching values from cements with fly ash approach within an order of magnitude of the SQD limit. Furthermore, in the case of selenium, maximum release from fly ash amended materials exceeded the limit value for unrestricted use by about 20%; however, the selenium maximum release value is based on a limited number of data and should be confirmed over a broader range of data. Furthermore, comparison with regulatory criteria for The Netherlands should not be taken to imply regulatory criteria for the United States.

The impact of carbonation on the monolith test results for a single set of samples also is presented separately as Appendix E. Notably, carbonated samples of CEM I cement mortars had increased leaching of arsenic relative to the uncarbonated sample and the carbonated CEM II/B-V cement mortar had the greatest observed release of arsenic within this data comparison set. This is consistent with other studies on cement stabilized materials that indicated that carbonation resulted in a shift in arsenic release as a function of pH and much higher arsenic leaching concentrations (Garrabrants et al., 2004). Carbonated CEM I cement mortar had greater leaching of copper, antimony and vanadium compared to the corresponding uncarbonated mortars. CEM I carbonated samples had reduced leaching for barium, cadmium and nickel, while no significant change for chromium, molybdenum and zinc. Carbonation of CEM II/B-V cement mortars seem to result in somewhat increased leaching of vanadium and zinc and somewhat decreased leaching of barium and chromium of arsenic, antimony, copper and vanadium

relative to the corresponding noncarbonated samples. These observations suggest that the possibility of increased leaching of arsenic and vanadium during aging and recycling or disposal of cement should be carefully considered.

#### Comparison of CBP Cement Grout, Mortar and Concrete with Fly Ash (US data)

Results of the leaching comparisons for the CBP mortar, grout and concrete are provided in Appendix F and Appendix G for pH-dependent leaching and monolith leaching, respectively. Based on pH-dependence, the fly ash (FAF) source material resulted in significantly higher leaching concentrations of arsenic, boron, cadmium, molybdenum, antimony, selenium and vanadium than the grout (BGM), mortar (SVC) and concrete (VCT). The higher leaching observed from fly ash than from fly ash amended cement materials appears to be the result of significant chemical interaction (e.g., adsorption and mineral precipitation) of arsenic, cadmium, selenium and antimony with the cementitious matrix, whereas the observed higher leaching in fly ash of boron, molybdenum and vanadium appear to be primarily the result of fly ash dilution in the cement matrix. Chromium concentrations are lower in the cement materials, most likely because of the reducing characteristics of formulations containing blast furnace slag. Leaching of beryllium, cobalt, copper, nickel, lead, thallium and zinc is essentially the same for both the fly ash and cement materials, except for thallium in SVC which was below detection limits.<sup>9</sup> Barium and uranium leaching was less from the fly ash than from the cement as a result of the higher content of these constituents in portland cement. For all of the evaluated constituents except arsenic at pH less than 6, leaching as a function of pH from the CBP cement materials was either consistent with or less than the observed leaching from the EU mortars and concrete samples containing fly ash as shown by the 90 percent confidence intervals for CEM II/V-B samples superimposed on the CBP material figures.

Monolith leaching results indicated that cumulative release from the CBP cement materials was within or less than the range observed for the EU samples containing fly ash (90 percent confidence intervals for CEM II/V-B samples). The increase in cumulative lead release for BGM after approximately two days is unknown.

#### Comparison of Cement Admixture Paste Containing Fly Ash

Results of the leaching comparisons for the cement admixture paste containing fly ash (MBD2) are provided in Appendix H and Appendix I for pH dependent leaching and monolith leaching, respectively. For pH dependent leaching, greater leaching of antimony, cobalt, copper, nickel and selenium was observed from admixture pastes than from the fly ash, which may be the result of contributions of these constituents from the steel slag whereas greater leaching of barium is likely from portland cement.<sup>10</sup> Chromium leaching was decreased in the cement admixture paste compared to the fly ash which is likely

---

<sup>9</sup> The likely reason for non-detected values for thallium for sample SVC is unknown.

<sup>10</sup> Although the steel slag used in this study was not characterized separately, elevated leaching of antimony, cobalt nickel and selenium has been indicated from characterization of other steel slag samples. Barium is a common constituent in Portland cement.

the result of the reducing properties of the cement admixture due to the addition of steel slag.<sup>11</sup> The reduction in leaching of molybdenum and vanadium in the cement admixture paste is likely the result of dilution of the fly ash in the cement material. Comparison to the superimposed mean and 90% confidence intervals for CEM II/V-B samples showed that the leaching from the cement admixture paste was greater than that for the EU mortars and concrete samples containing fly ash for arsenic, boron, cadmium, nickel (slightly), selenium and vanadium (at pH < 6). However, these observations may be a consequence of the addition of the steel slag rather than the fly ash. The leaching of the other constituents was either consistent with or less than the EU mortars and concretes.

Monolith leaching results indicated that cumulative release from the cement admixture paste was within or less than the range observed for the EU samples containing fly ash (90 percent confidence intervals for CEM II/V-B samples) for all constituents except iron for which EU data were available. Iron leaching likely was increased because of the strongly reducing nature of the matrix as a result of steel slag usage in the formulation.<sup>12</sup>

#### Comparison of Studied Fly Ash Samples with Other Fly Ash Characterization

Appendix J presents results of pH-dependent leaching of the fly ashes (FAF and CFA2) used in the cement materials described above in comparison with the 5<sup>th</sup> and 95<sup>th</sup> percentiles of leaching concentrations from the set of fly ash samples (35 samples) evaluated by USEPA as part of a study on characterization of coal combustion residues (Kosson et al., 2009)<sup>13</sup>. This comparison indicates that sample FAF had greater leaching for arsenic (3<pH<10), selenium (4<pH<6) and vanadium (4<pH<9) than the range of previously characterized samples while sample CFA2 had greater leaching for arsenic (pH = 7) and vanadium (4 < pH < 9) than the range of previously characterized samples. All other constituents were consistent with the ranges from the previously characterized samples.

#### Comparison of Single Extraction Leaching Test Results (US and Canadian data) with pH Dependence Leaching Test Results and Health Based Numbers

Figure 3 presents an annotated example single COPC graph comparing results from single extraction leaching tests (blue squares, green dots, red filled triangles) and the median (black dashed line) and 90 percent confidence interval (gray dashed lines) from the EU CEM II/V-B cement mortars and concretes containing fly ash. The pH domain of 7-13, considered appropriate for portland cement-based materials based on typical initial pore water pH of ca. 13 and fully carbonated and leached systems with pH >7, is indicated using vertical red dashed lines<sup>14</sup>. Results less than the applicable analytical method detection limit (MDL) are indicated in red using open symbols when variable MDLs were used in a study, or as a

---

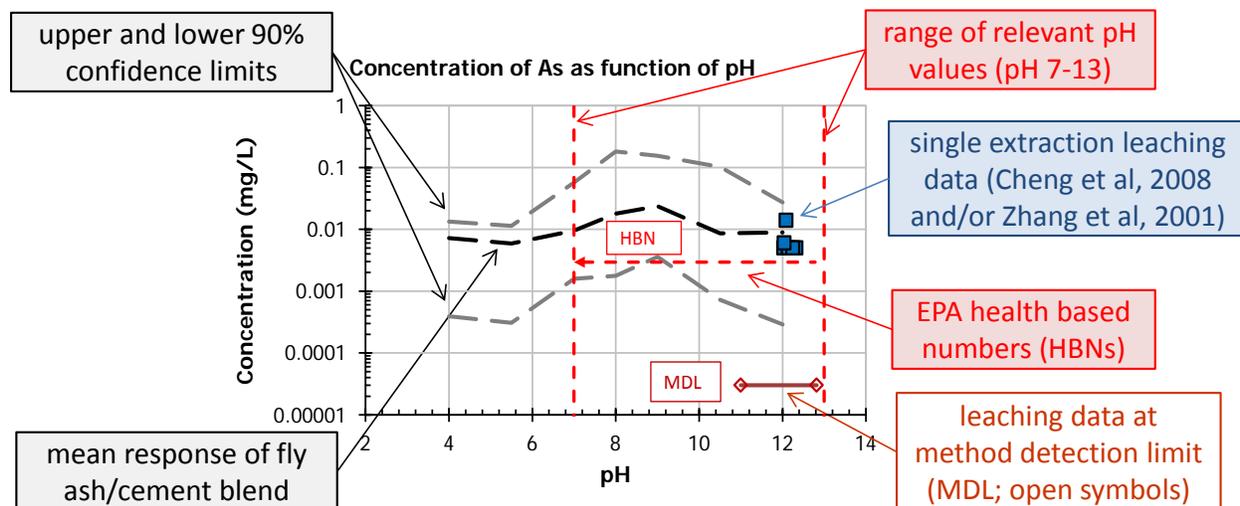
<sup>11</sup> In this matrix, steel slag was added because of its reducing properties with the intention of increasing retention of technetium in nuclear waste management applications. The steel slag used was not available for separate leaching characterization.

<sup>12</sup> Iron(II) is considerably more soluble than iron(III) at neutral to alkaline pH.

<sup>13</sup> This report provides leaching characterization of 35 fly ash samples obtained from 22 US facilities with a range of coal types being burned and air pollution control systems that may impact fly ash characteristics.

<sup>14</sup> Lower initial pore water pH values (e.g., pH ca. 11) are associated with some portland cement mixtures with significant amounts of admixture materials (e.g., some type of fly ash). Narrower pH ranges may be applicable for specific cement and concrete materials under well-defined environmental exposure conditions.

bar over the observed pH range for a single MDL. Leaching test results are also compared to health based numbers (HBNs, red dashed line) used as a reference threshold for the constituent of interest<sup>15</sup>. However, COPC leaching in this representation are estimates of liquid-solid partitioning (or equilibrium) concentrations that may potentially leach from cement materials containing fly ash without accounting for the physical form or the material (i.e., a monolithic material with low permeability with a tortuous pore structure through which COPCs must transport to the surface of the material prior to release).



**Figure 3. Annotated graph showing leaching data relative to health based numbers (HBNs) over a relevant pH range for cementitious materials.**

Any assessment of the environmental impact of these releases also needs to consider the dilution and attenuation of these constituents in run off, transport through the vadose zone and in ground water, and the plausibility of drinking water well contamination resulting from the release. Dilution and attenuation factors (DAFs) for metals have been estimated to be potentially as low as 2 to 10 on a national basis or as high as 8,000 at a particular site with hydrogeology that indicated low transport potential<sup>16</sup>. Therefore, comparison with thresholds greater than the HBN and developed for specific scenarios may be appropriate. Selected results from single extraction leaching tests (Cheng et al., 2008 and Zhang et al., 2001) are compared with the median and 90 percent confidence intervals from the EU CEM II/V-B cement mortars and concretes containing fly ash in Figure 4 and Figure 5 using the nomenclature illustrated in Figure 3; a full set of comparisons is provided in Appendix K. Results of the single extraction leaching tests are consistent with the corresponding results obtained from pH

<sup>15</sup> The HBN for each COPC is derived as the lower value of the allowable concentration based on the scenario either of (i) drinking water ingestion or (ii) fish ingestion. The relevant threshold value for each scenario is based on the median exposure for children age 1 through adult, with either a lifetime excess cancer risk of  $1 \times 10^{-5}$  or a hazard quotient of 1.

<sup>16</sup> See 60 FR 66372, December 21, 1995, for a discussion of model parameters leading to low DAFs, particularly the assumption of a continuous source landfill. Implied DAFs for the metals of interest here can be found at 60 FR 66432-66438 in Table C-2. Site specific high-end DAFs are discussed in 65 FR 55703, September 14, 2000.

dependent leaching tests with the exceptions of barium, calcium, strontium and potassium, where lower leaching concentrations from the single extraction tests are likely the consequence of partial carbonation of the samples during preparation and testing (Garrabrants et al., 2004). Many of the test results were less than the analytical MDLs reported for the corresponding study. Reported MDLs are indicated on the respective constituent graphs as unfilled symbols.

A clear limitation of the single extraction batch tests is that the results provide insight into the leaching behavior only at a single pH and therefore do not allow for evaluation of leaching over the potential range of leaching pH conditions anticipated during the lifecycle of material use. In contrast, the pH dependence leaching test results provide insights into where leaching is anticipated to decrease, increase or remain the same as the material changes in response to aging and environmental conditions. This information is most effectively used in conjunction with results from mass transfer leaching tests (i.e., monolith diffusion leaching test such as Method 1315 or NEN 7345, CEN/TC 351 TS-2 or CEN/TS 15863)

HBNs are also compared with the leaching test results in Figure 4 and Appendix K. This comparison indicates that HBNs are exceeded at the mean concentration for pH dependent leaching over the pH domain of 7 to 13 by arsenic, chromium and cobalt. HBNs are exceeded by the 90 percent confidence interval additionally by molybdenum, lead, antimony, selenium, strontium and vanadium. The ratio of the maximum value over the pH domain (7-13) of the 90 percent confidence interval to the corresponding HBN is provided in Table 5. Values less than one indicate the expected leaching concentration from pH dependent leaching tests is always expected to be less than the HBN. As indicated earlier, the comparison of pH dependent leaching test results to HBNs does not consider reductions in leaching concentrations resulting from the physical form of the material, nor dilution and attenuation from the point of release at the material interface to the point of compliance (e.g., a down-gradient aquifer or drinking water well). Thus, when the physical form of the material and the range of dilution and attenuation factors are considered, a very large fraction of the cases are likely to not have adverse impacts to human health based on current HBNs. The ratio of the mean or maximum value to the HBN provided in Table 5 provides an indication of the dilution and attenuation factor as a result of the physical form of the material or natural conditions from the location of material use to the point of compliance that would be needed to avoid adverse impact for the indicated fraction of the cases. These results also indicate that the constituents in fly ash most likely to limit usage rates of fly ash in concrete and other cement products are antimony, arsenic, chromium, cobalt and molybdenum because the ratio of the maximum value over the pH domain divided by the respective HBN is greater than 10.

The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes

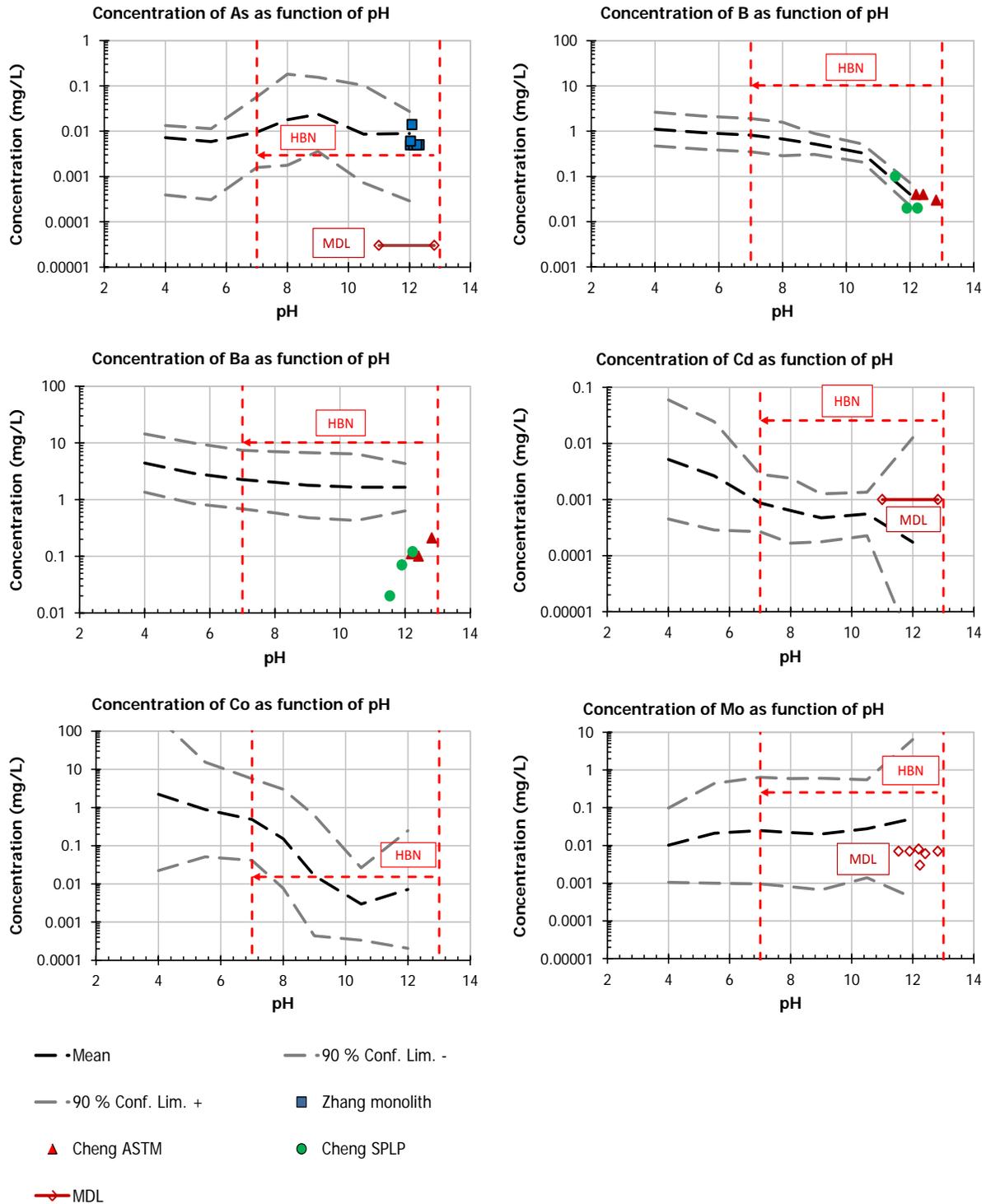


Figure 4. Statistical representation (mean with 90% confidence limits) of concentrations of the EU CEM II/V-B cement mortars and concretes containing fly ash and literature single extraction test results (Cheng et al., 2008; Zhang et al., 2001) compared to health based numbers (HBNs) over a relevant pH range of 7 to 13.

The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes

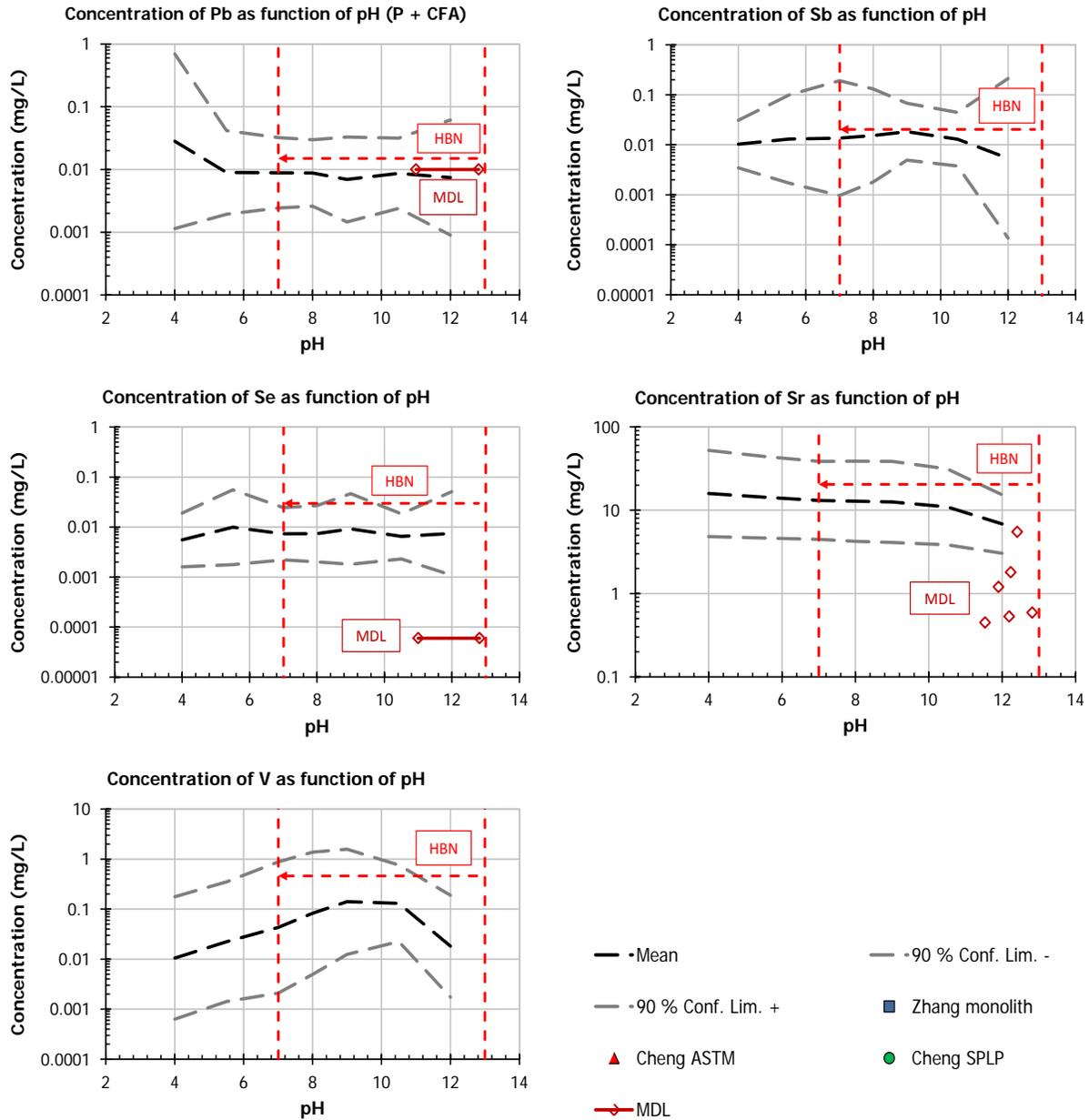


Figure 5. Statistical representation (mean with 90% confidence limits) of concentrations of the EU CEM II/V-B cement mortars and concretes containing fly ash and literature single extraction test results (Cheng et al., 2008; Zhang et al., 2001) compared to health based numbers (HBNs) over a relevant pH range of 7 to 13.

**Table 5. Comparisons of the ratio of the maximum value of the 90 percent confidence interval to the HBN (Max/HBN) and the maximum value of the mean values to the HBN (Mean/HBN).**

Constituent	HBN (mg/L)	Ratio Max/HBN	Ratio Mean/HBN	Constituent	HBN (mg/L)	Ratio Max/HBN	Ratio Mean/HBN
Aluminum	51	0.23*	0.01	Iron	35.7	0.10	0.0086
Antimony	0.0204	10	0.89	Lead	0.015	4.0	0.59
Arsenic	0.00294	61	8.0	Manganese	2.40	6.3	0.34
Barium	10.2	0.73	0.22	Molybdenum	0.255	25	0.20
Boron	10.2	0.19	0.08	Nickel	1.02	1.1	0.17
Cadmium	0.0255	0.50	0.034	Selenium	0.0299	1.6	0.31
Chromium	0.00881	730	54	Strontium	20.4	1.9	0.63
Cobalt	0.0153	370	32	Vanadium	0.459	3.4	0.28
Copper	0.51	1.8	0.025	Zinc	6.48	0.016	0.004

**Notes:**

This comparison does not consider the dilution and attenuation of these constituents in run off, transport through the vadose zone and in ground water, and the plausibility of drinking water well contamination resulting from the release.

\*For aluminum only, the single extraction leaching test results were greater than the 90% confidence interval and therefore the maximum single extraction leaching test result was used in the ratio.

## **Conclusions**

The available data suggest that the use of coal combustion fly ash in cement materials, for different combinations of fly ash source and usage rates, will not increase leaching of some constituents to levels greater than typical ranges for cement materials not containing fly ash. However, there are data limitations that preclude making broad based claims for some usage rates and fly ashes including those resulting from changes in air pollution control at coal-fired power plants. Based on available data (31 cement mortar and concrete samples containing coal fly ash in comparison to 21 cement and mortar samples that did not contain coal fly ash), results indicate that some (and likely a large portion) of coal fly ashes can be used in cement and concrete formulations without causing a greater range in leaching of COPCs than observed from analogous cement materials not containing fly ash and without causing adverse environmental and health impacts. The range of fly ash sources and usage rates for cement materials with pH dependent and monolith leaching test data available is more limited than the full range of typical fly ash usage rates and typical fly ash leaching behavior. In addition, the data evaluated in this report does not consider changes in leaching from cement-based materials that may occur if the characteristics of coal fly ash used in cement-based materials change in response to recent changes in air pollution control requirements at coal fired power plants. To the extent that such changes affect the fly ash characteristics, the available data sets do not allow evaluation of the impacts of the following potential changes to air pollution controls at coal fired power plants: (i) addition of activated carbon or halogenated activated carbon, (ii) a shift in the coal types burned or blends thereof to achieve new air pollution control limits, (iii) presence or increase in ammonia in the ash because of excess ammonia injected as part of SCR NO<sub>x</sub> controls, and (iv) the inclusion of sorbent from use of dry sorbent injection systems (i.e., trona (sodium sesquicarbonate), sodium carbonate or hydrated lime).

Based on the evaluation of available data for the leaching of cement mortars and concrete with and without partial replacement of cement with coal combustion fly ash, the following observations can be made:

- The leaching behavior of individual constituents from cement mortars and concrete made with coal fly ash exhibits characteristic leaching concentration as a function of pH behavior that is controlled by the cement chemistry.
- When leaching is compared between cement mortars and concrete with and without coal fly ash, cement mortars and concrete containing fly ash had somewhat higher upper bounds for the ranges of leached concentrations for barium, cobalt, copper, molybdenum, phosphorus, antimony, silicon (at pH > 6) and vanadium (at 4 < pH < 8) based on pH dependent leaching tests (with the expected field pH to range from 7 to 13). Based on monolith leaching tests, higher upper ranges of leaching were observed in some cases containing fly ash only for boron, cadmium and molybdenum.
- In comparison to Dutch national criteria for leaching from construction materials, only selenium approached or exceeded the limit value for unrestricted beneficial use in one case out of seventeen. In addition to selenium, only maximum values for antimony and cadmium were within an order of magnitude of the Dutch regulatory limits.

- USEPA HBNs were exceeded at the median concentration for pH dependent leaching over the pH domain of 7 to 13 by arsenic, chromium and cobalt. HBNs are exceeded by the 90 percent confidence interval additionally by molybdenum, lead, antimony, selenium, strontium and vanadium. However, the comparison of pH dependent leaching test results to HBNs does not consider reductions in leaching concentrations resulting from the physical form of the material, nor dilution and attenuation from the point of release at the material interface to the point of compliance (e.g., a down-gradient aquifer or drinking water well).
- Leaching of COPCs from fly ash was not significantly increased by incorporation of the fly ash in cement materials, based on comparison between leaching test results of fly ash alone and fly ash in cement materials. This suggests that use of fly ash in concrete will not increase the overall leaching of COPCs from fly ash into the environment.
- Arsenic leaching from fly ash was decreased for several cases by incorporation into cement materials. Also, chromium leaching is decreased when reducing materials (such as ground granulated blast-furnace slag) are used as part of the cement material formulation.
- Using the pH dependent and monolith leaching test data, as described in the LEAF methodology, provides a more robust approach than single point leaching tests for evaluating the potential environmental and health impacts from use of coal fly ash in cement and concrete materials because LEAF considers the likely range of leaching pH over the material's lifecycle and the physical form of the materials (i.e., monolithic). Single extraction leaching tests cannot adequately describe the leaching characteristics of COPCs accounting for the likely environmental pH domain and physical form.

This study should be viewed as the beginning of a collection of robust leaching characterizations for fly ash and fly ash amended cementitious materials, high fly ash replacement materials such as solidification/stabilization formulations, and other utilization applications. It is prudent to develop a characterization and quality control program to determine which combinations of fly ash and cement formulations have leaching characteristics within the typical range for cement materials without fly ash.

Furthermore, without comparison to risk-informed criteria, potential increases in leaching of some COPCs, demonstrated through direct comparisons between materials with and without fly ash, does not indicate that the use of fly ash as a supplemental cementitious material will result in adverse impacts to human health or the environment. Thus, the approach taken in this report should be used to develop an evaluation basis (e.g., thresholds, regulatory guidance structure, and quality control program) for the acceptability of leaching characteristics greater than the typical range for cement-based materials without fly ash. The systematic behavior of COPC leaching from cement materials produced using fly ash will allow determination of the general coal sources and coal combustion facility configurations that result in ash that is acceptable for use at intermediate or high usage rates (i.e., 10-30 wt% or up to 50% of the cement dry mixture), and reduce the extent of needed quality control testing.

## References

Aalbers, Th. G., P.G.M. de Wilde, G.A. Rood, P.H.M. Vermij, R.J. Saft, A.I.M. van de Beek, M.H. Broekman, P. Masereeuw, Ch. Kamphuis, P.M. Dekker and E.A. Valentijn (1993) Milieuhygiënische kwaliteit van primaire en secundaire bouwmaterialen in relatie tot hergebruik en bodem – en oppervlaktewaterenbescherming, RIVM 771402006, RIVM, Bilthoven, the Netherlands, December 1993.

ACAA (2012). 2010 Coal Combustion Product (CCP) Production & Survey, American Coal Ash Association, [http://acaaffiniscape.com/associations/8003/files/2010\\_CCP\\_Survey\\_FINAL\\_102011.pdf](http://acaaffiniscape.com/associations/8003/files/2010_CCP_Survey_FINAL_102011.pdf) (accessed 25 August 2012).

Arnold, J., D.S. Kosson, H. van der Sloot, R. DeLapp, P. Seignette, A.C. Garrabrants and K. Brown (2010). Characterization of Reference Materials and Related Materials for the Cementitious Barriers Partnership, CBP-TR-2010-012-1 (available at [www.cementbarriers.org](http://www.cementbarriers.org)).

ASTM Standard D3987-85 (1985). Standard Test Method for Shake Extraction of Solid Waste with Water, ASTM International, West Conshohocken, PA, 1985.

Building Materials Decree (1995). Staatsblad van het Koninkrijk der Nederlanden 567, pp. 92 (in Dutch)

CEN/TS 14429 (2005). Characterization of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with Initial Acid/base Addition, CEN, Brussels, Belgium.

CEN/TS 14997 (2005). Characterization of Waste – Leaching Behaviour Tests – Influence of pH on Leaching with continuous pH control, CEN Technical Committee TC 292.

CEN/TS 15863 (2009). Characterization of waste – Leaching Behaviour Tests – Dynamic Monolithic Leaching Test with Periodic Leachant Renewal, CEN Technical Committee TC 292.

CEN/TS-2 (2009). Generic Horizontal Up-flow Percolation Test for Determination of the Release of Substances from Granular Construction Products, CEN Technical Committee TC 351.

Cheng, C.-M., P. Taerakul, W. Tu, B. Zand, T. Butalia, W. Wolfe, and H. Walker (2008). Surface runoff from full-scale coal combustion product pavements during accelerated loading, *Journal of Environmental Management*, p591-599.

ECN (2000). Unpublished data, The Energy Research Centre of The Netherlands, Petten, The Netherlands.

EN 196-1 (2005). Methods of testing cement - Determination of strength, CEN, Brussels, Belgium.

Federal Register 75:118 (June 21, 2010). Hazardous and Solid Waste Management System; Identification and Listing of Special Wastes; Disposal of Coal Combustion Residuals from Electric Utilities,” pp. 35,127-35,264.

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes*

Garrabrants, A.C., F. Sanchez and D.S. Kosson (2004). Changes in constituent equilibrium leaching and pore water characteristics of a Portland cement mortar as a result of carbonation. *Waste Management* 24:19-36.

Garrabrants, A.C., R.C. DeLapp, and D.S. Kosson (2008). Leaching Results and Interpretation of Constituent Release from Representative Low-Activity Waste Treated with Reducing Grout: CRESP III Report, Consortium for Risk Evaluation with Stakeholder Participation, December 2007 (available at [www.CRESP.org](http://www.CRESP.org)).

Garrabrants, A.C., D.S. Kosson, L. Stefanski, R. DeLapp, P.F.A.B. Seignette, H.A. van der Sloot, P. Kariher, and M. Baldwin (2012a). Interlaboratory Validation of the Leaching Environmental Assessment (LEAF) Method 1313 and Method 1316, EPA-600/R-12/623, US Environmental Protection Agency, Washington DC.

Garrabrants, A.C., D.S. Kosson, R. DeLapp, P. Kariher, P.F.A.B. Seignette, H.A. van der Sloot, L. Stefanski, and M. Baldwin (2012b). Interlaboratory Validation of the Leaching Environmental Assessment (LEAF) Method 1314 and Method 1315, EPA-600/R-12/624, US Environmental Protection Agency, Washington DC.

Kosson, D.S., F. Sanchez, P. Kariher, L.H. Turner, R. DeLapp, and P. Seignette (2009). Characterization of Coal Combustion Residues from Electric Utilities – Leaching and Characterization Data, EPA-600/R-09/151, U.S. Environmental Protection Agency, Air Pollution Prevention and Control Division, December 2009.

Kosson, D.S., H.A. van der Sloot, F. Sanchez and A.C. Garrabrants (2002). An integrated framework for evaluating leaching in waste management and utilization of secondary materials, *Environmental Engineering Science*, 19(3), 159-204.

NEN 7345 (1994). Leaching Characteristics of Soil and Stony Building and Waste Materials – Leaching Tests – Determination of the Leaching of Inorganic Components from Building and Monolithic Waste Materials with Diffusion Tests, NNI, Delft, the Netherlands

Schiessl, P. (1997). Harmonization of leaching/extraction tests for construction materials, WASCON 1997, The 3rd International Conference on the Environmental and Technical Implications of Construction with Alternative Materials. *Putting Theory into Practice*, Series in Environmental Science 71, Elsevier, The Netherlands.

Soil Quality Decree (Regeling bodemkwaliteit), Staatscourant, December 2007, 247, p. 67 (in Dutch).

USEPA (1992a). SW-846 Method 1311 Toxicity Characteristic Leaching Procedure, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*, US Environmental Protection Agency, <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf>.

USEPA (1992b). SW-846 Method 1312 Synthetic Precipitation Leaching Procedure, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*, US Environmental Protection Agency, <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1312.pdf>.

USEPA (2011). QAPP for the EPA Interlaboratory Validation Study of Proposed SW846 Leaching Methods. Quality Assurance Project Plan, Category III/Technology Development, Project No: RN990272.0007.

van der Sloot, H.A., E.G. Weijers, D. Hoede and J. Wijkstra (1985). Physical and Chemical Characterization of Pulverized Coal Ash with Respect to Cement-based Applications, ECN-178, Netherlands Energy Research Foundation, Petten, the Netherlands.

van der Sloot, H.A. and E.G. Weijers (1987). Physikalische und chemische Kenndaten von 50 Kohlenstaubaschen mit Blick auf die Verwendung als Betonzusatzstoff, *VGB Kraftwerkstechnik* 67(5), 527-534.

van der Sloot, H.A., G.J.L. van der Wegen, D. Hoede and G.J. de Groot (1994). Intercomparison of leaching tests for stabilized waste. In: Environmental aspects of Construction with waste materials. Eds. J.J.J.M. Goumans, H.A. van der Sloot, and Th.G. Aalbers, Elsevier Science Publishers, Amsterdam, 63-76.

van der Sloot, H.A., G.J.L. van der Wegen, D. Hoede, G.J. de Groot and Ph. Quevauviller (1995). Intercomparison of leaching tests for stabilized waste. Commission of the European Communities, EUR 16133 EN, 1995.

van der Sloot, H.A., and D. Hoede (1997) Long-term leaching behaviour of cement mortars, ECN-C-97-042, ECN, the Netherlands.

van der Sloot, H.A., Hoede, D., Rietra, R.P.J.J. (1998) Leaching behaviour of artificial aggregates - EU project BRST-CT98-5234, ECN-C--01-014, ECN, the Netherlands.

van der Sloot, H.A. (2000). Comparison of the characteristic leaching behaviour of cements using standard (EN 196-1) cement-mortar and an assessment of their long-term environmental behaviour in construction products during service life and recycling, *Cement and Concrete Research* 30, 1079-1096.

van der Sloot, H.A., D. Hoede, R.P.J.J. Rietra, R. Stenger, Th. Lang, M. Schneider, G. Spanka, E. Stoltenberg-Hansson, and A. Lerat (2001a). Environmental Criteria for Cement-based Products, ECRICEM I, ECN C-01-069, Netherlands Energy Research Foundation, Petten, the Netherlands.

van der Sloot, H.A., O. Hjelmar, J. Bjerre Hansen, P. Voitke, P. Lepom, R. Leschber, B. Bartet, N. Debrucker (2001b). Validation of CEN/TC 292 Leaching Tests and Eluate Analysis Methods PrEN 12457 part 1- 4, ENV 13370 and ENV 12506 in co-operation with CEN/TC 308. ECN-C-01-117.

van der Sloot, H.A. (2001c) ECN on Study for ENCI, personal communication.

van der Sloot, H.A., A. van Zomeren, R. Stenger, M. Schneider, G. Spanka, E. Stoltenberg-Hansson, and P., Dath (2008a). Environmental CRiteria for CEMent-based products (ECRICEM) Phase I: Ordinary Portland Cements and Phase II: Blended Cements, Executive Summary, ECN-E-08-011, Netherlands Energy Research Foundation, Petten, the Netherlands.

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Material on The Leaching of Constituents from Cements and Concretes*

van der Sloot, H.A., P.F.A.B. Seignette, J.C.L. Meeussen, O. Hjelm, and D.S. Kosson (2008b). A database speciation modelling and decision support tool for soil, sludge, sediments, wastes and construction products: LeachXS™-Orchestra, in the *Second International Symposium on Energy from Biomass and Waste*, Venice, 17-20 November 2008.

van der Sloot, H.A. (2009) ECN on Quality Control of Cement, personal communication.

van der Sloot, H.A., van Zomeren, A., Meeussen, J.C.L., Hoede, D., Rietra, R.P.J.J., Stenger, R., Lang, Th., Schneider, M., Spanka, G., Stoltenberg-Hansson, E., Lerat, A., Dath, P. (2011) Environmental criteria for cement based products ECRICEM. Phase I: Ordinary Portland Cement & Phase II: Blended Cements and methodology for impact assessment. ECN-E--11-020, ECN, the Netherlands

Verschoor, A.J., J.J.P. Lijzen, H.H. van den Broek, R.F.M.J. Cleven, R.N.J. Comans, and J.J. Dijkstra (2008) Revision of the Dutch Building Materials Decree: Alternative Emission Limit Values for Inorganic Components in Granular Building Materials in *Proceedings of 9th International Symposium on Environmental Geo-technology and Global Sustainable Development*, Hong Kong.

Zhang, M.H., M.C. Blanchette, and V.M. Malhotra (2001) Leachability of trace metal elements from fly ash concrete: Results of column-leaching and batch leaching tests. *ACI Materials Journal*, 98:126-136.

## **Appendix A. pH Dependent Leaching of EU Cement Mortars: CEM I (without fly ash) and CEM II/B-V (with fly ash)**

**Notes:**

- Gray dashed lines indicate 90 percent confidence intervals; black dashed lines indicate mean values.
- Circled values indicate “own pH” (end point pH when extracted with deionized water at 10 mL/g)
- Use of the same color for data sets indicates samples from the same facility taken at different times.

**Legend:**

<b>Sample name</b>	<b>Country</b>	<b>Description</b>	<b>Reference</b>
<b>Portland cements</b>			
Cement mortar CEM I B3	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B7	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D1	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B1	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N2	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N6	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B6	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B9	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D2	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N1	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N5	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM I N3	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM I TH1	Thailand	QC of cement by testing cement mortar	ECN, 2009

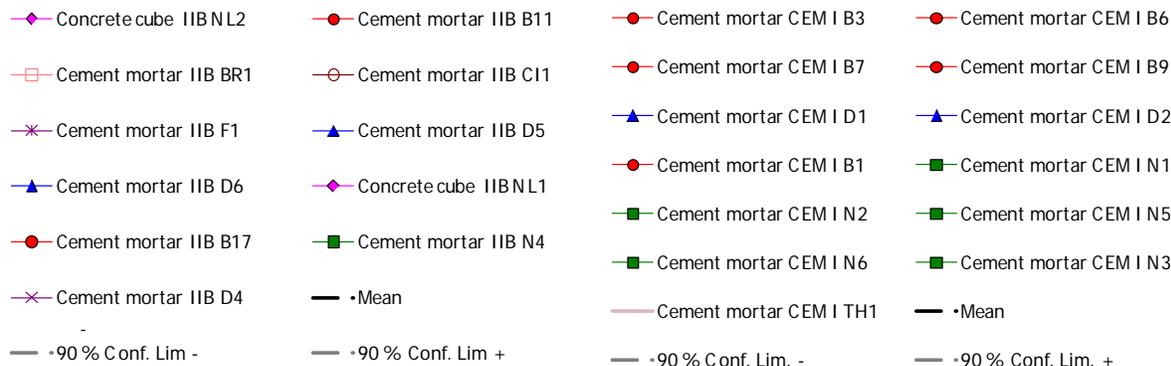
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

Sample name	Country	Description	Reference
<b>Blended cements with coal fly ash</b>			
Concrete CEM IIB NL2	Netherlands	Concrete cube, 20 % cement replacement by coal fly ash, carbonated by CO2 bubbling during leaching	ECN, 2001
Cement mortar CEM IIB B11	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM IIB BR1	Brazil	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM IIB CI1	Chile	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM IIB F1	France	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM IIB D5	Germany	Cement mortar with 20 % cement replacement	Van der Sloot et al., 2002
Cement mortar CEM IIB D6	Germany	Cement mortar with 20 % cement replacement	Van der Sloot et al., 2002
Concrete CEM IIB NL1	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash	ECN, 2001
Cement mortar CEM IIB B17	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM IIB N4	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1,2</sup>	van der Sloot et al., 2011
Cement mortar CEM IIB D5	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011

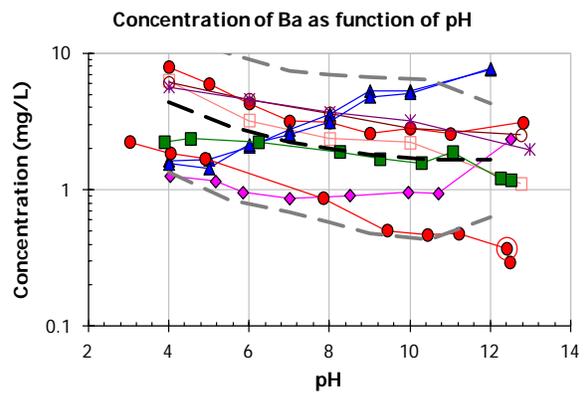
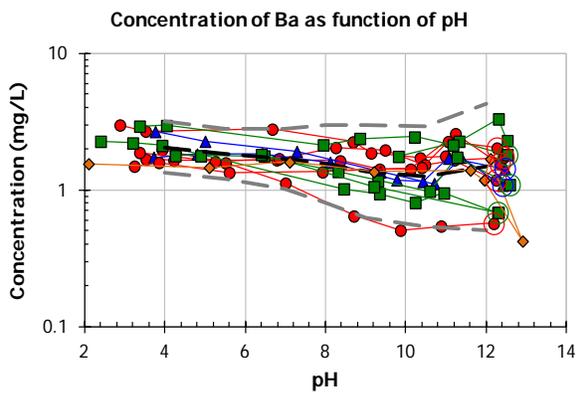
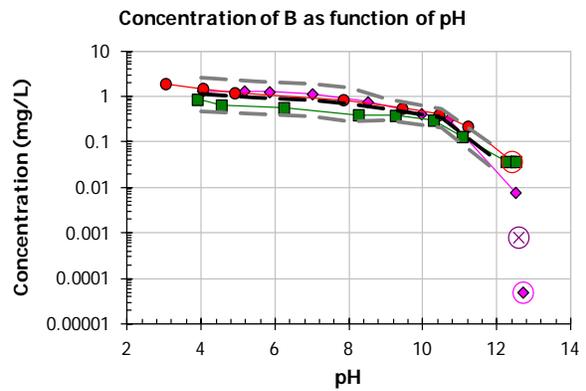
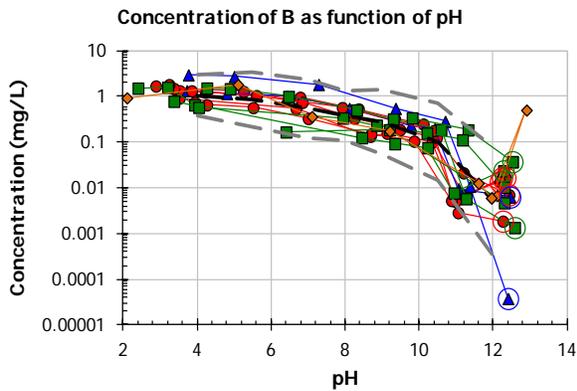
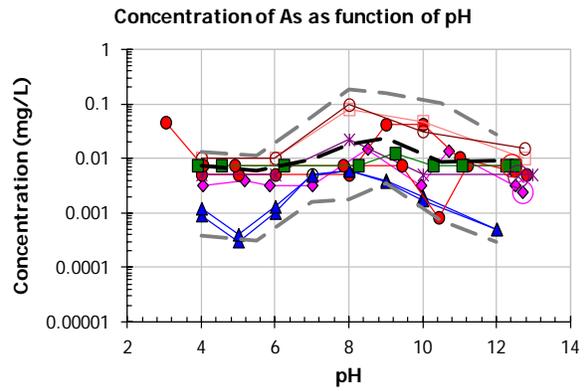
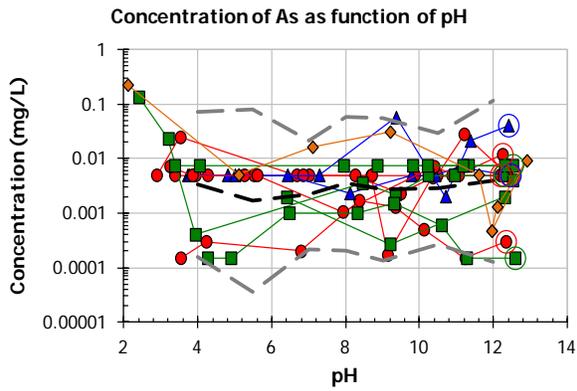
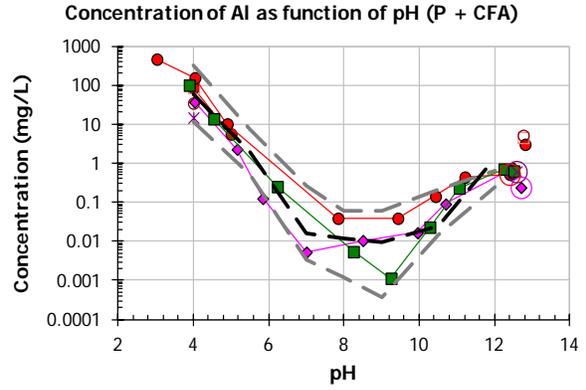
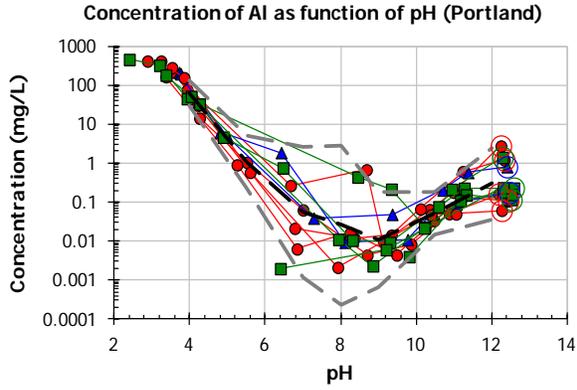
Note:

<sup>1</sup> After de-molding at the age of 24 hours, the mortar samples for the leaching tests were cured at 20 °C and 95 % relative humidity for another 27 days in plastic bags to prevent pre-leaching.

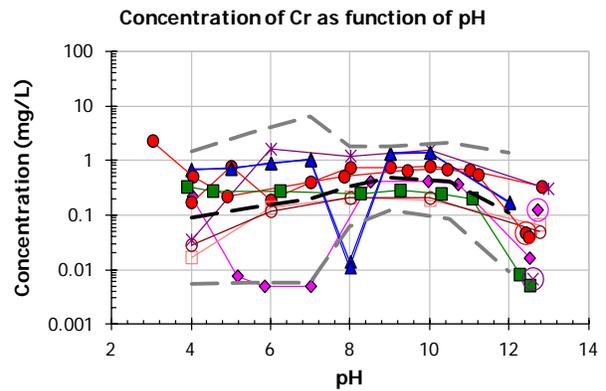
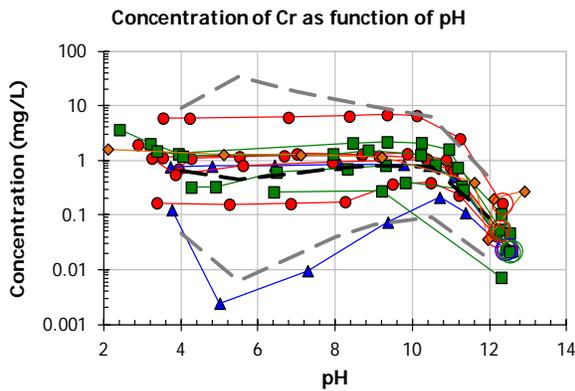
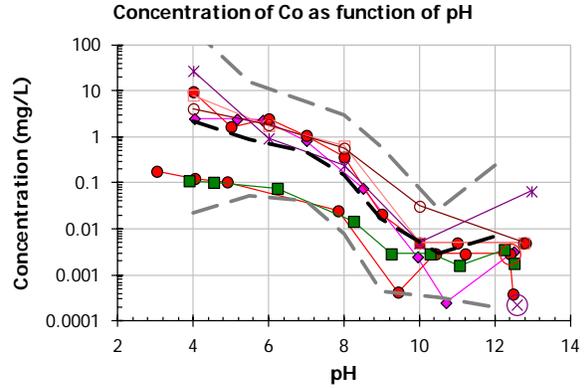
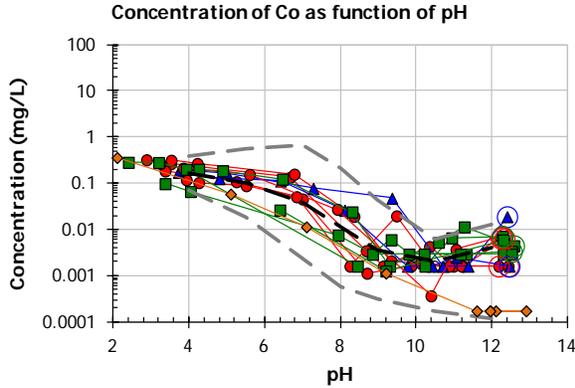
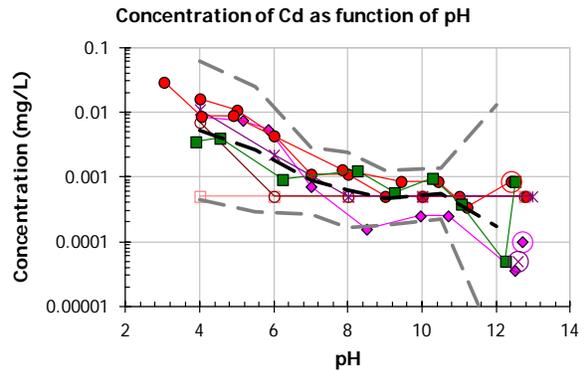
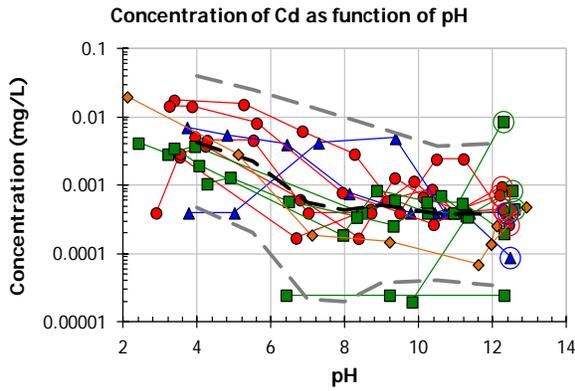
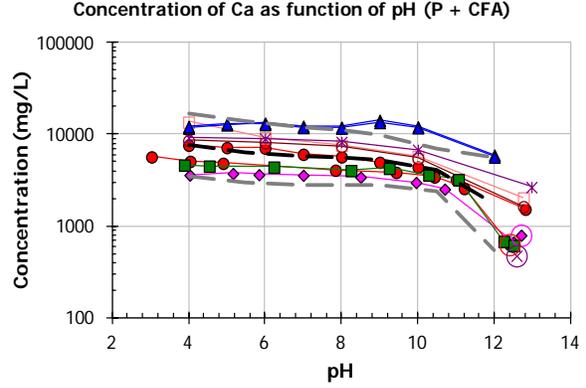
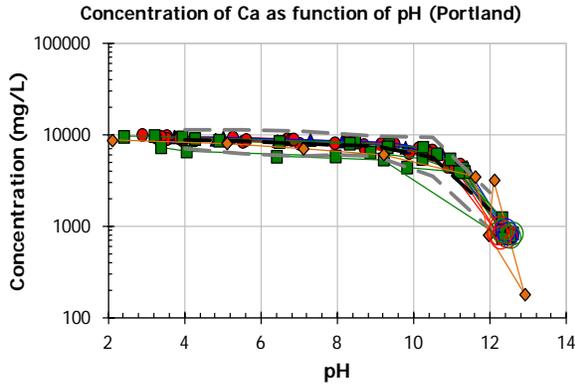
<sup>2</sup> The cement used in this mortar was type CEM II A-V rather than CEM II B-V. This minor distinction does not influence the observations or conclusions in this report.



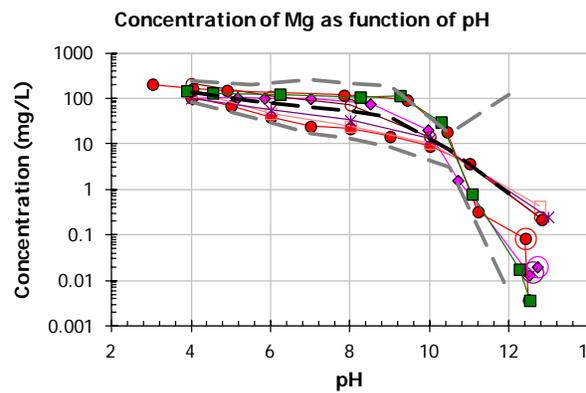
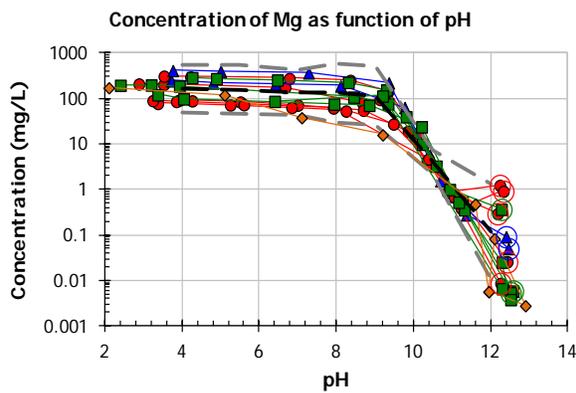
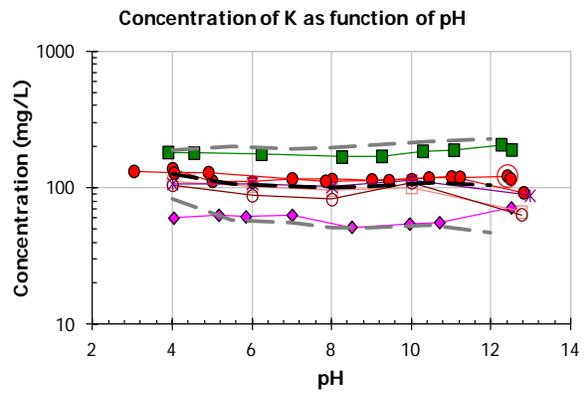
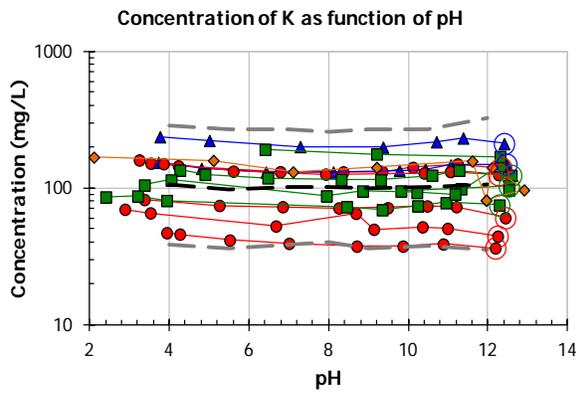
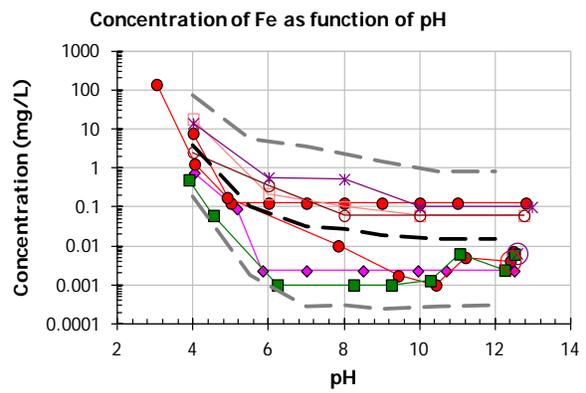
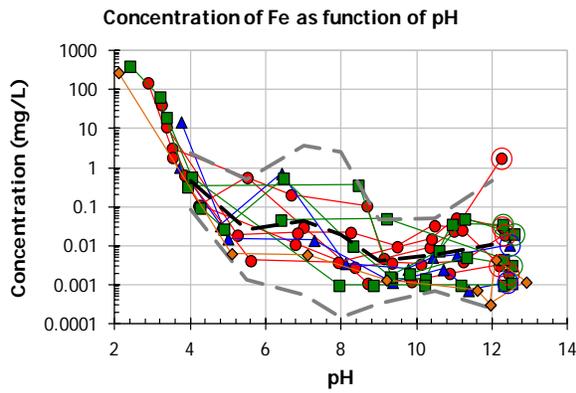
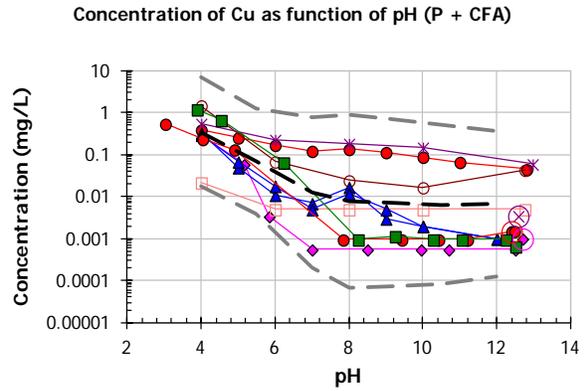
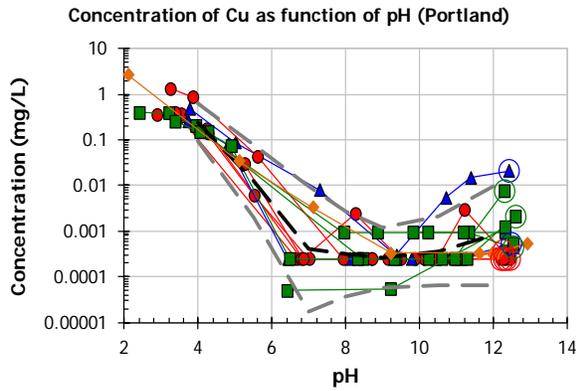
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



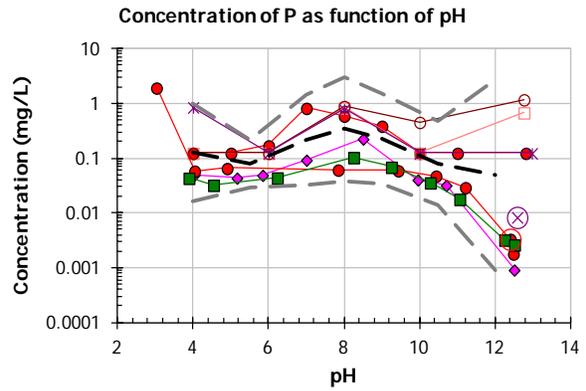
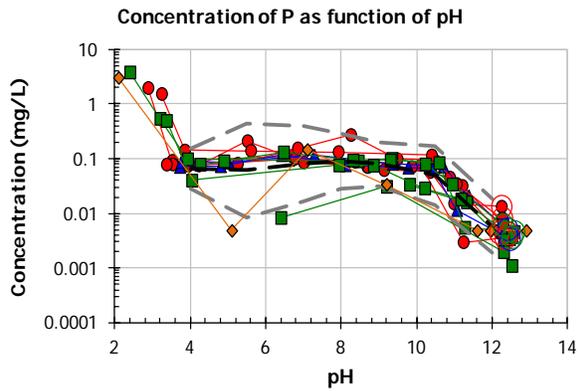
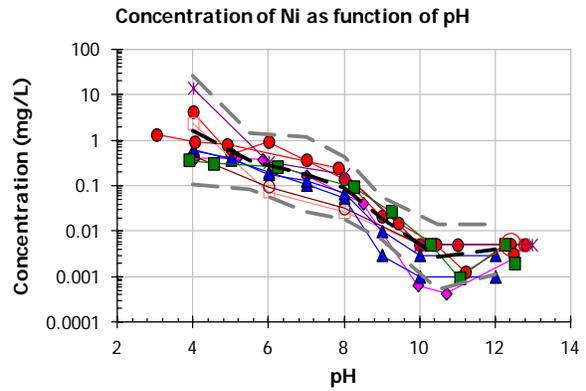
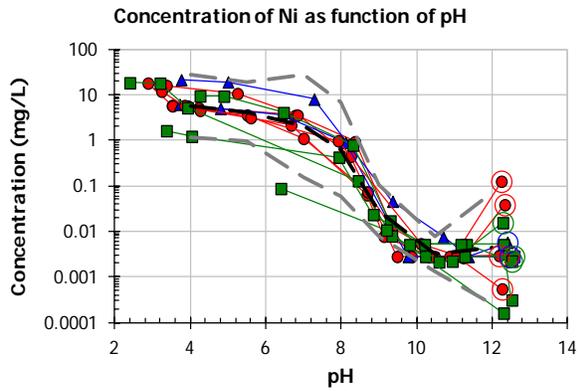
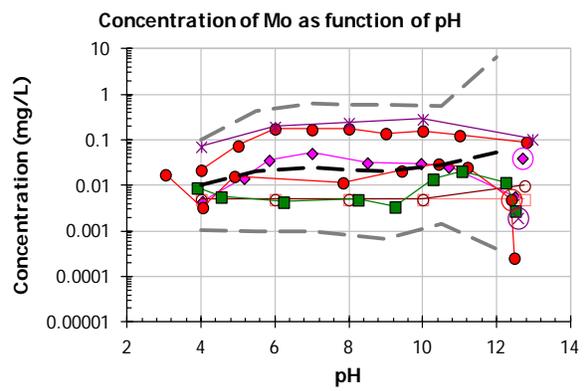
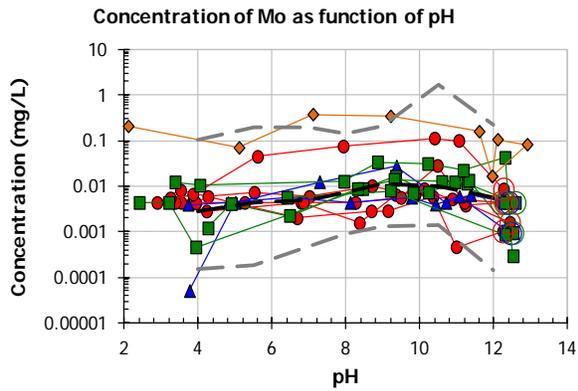
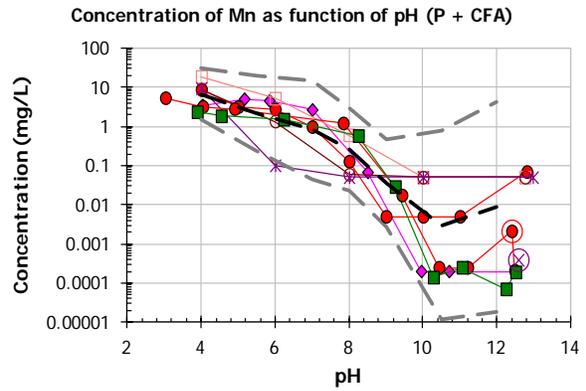
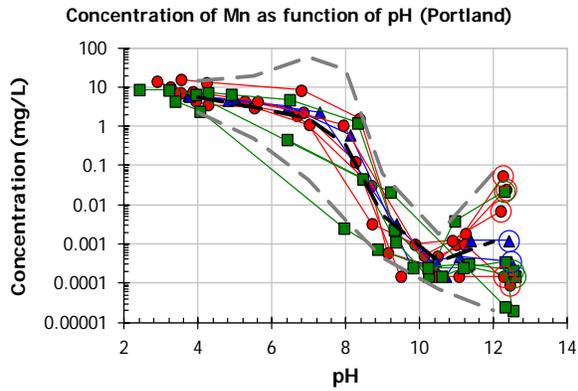
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



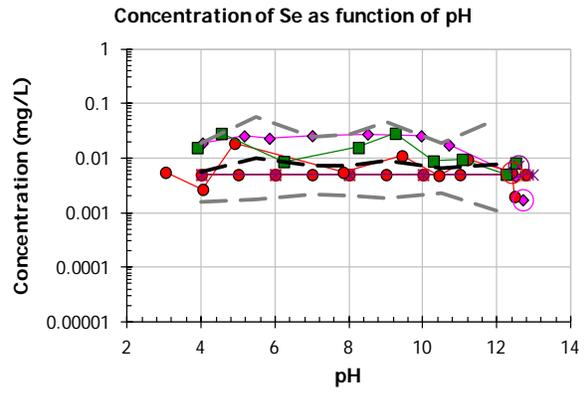
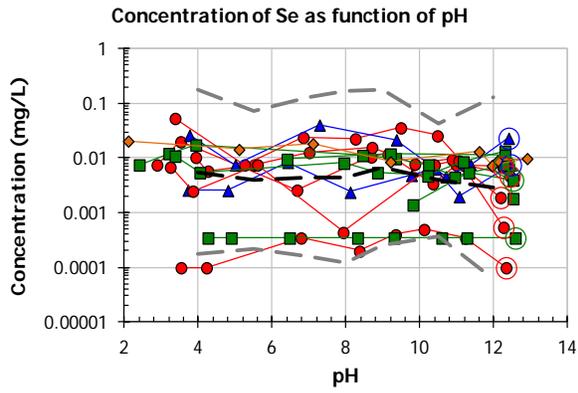
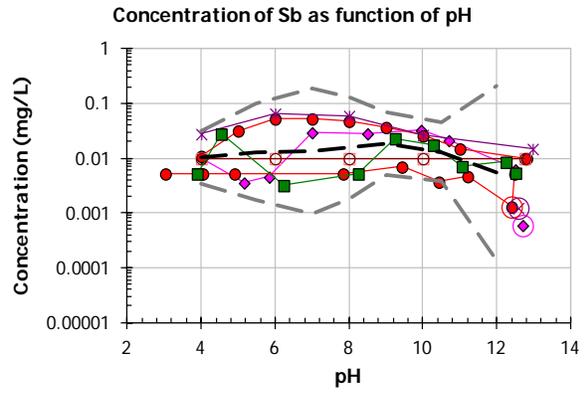
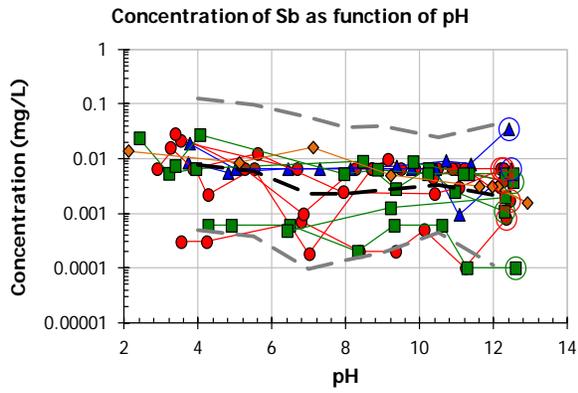
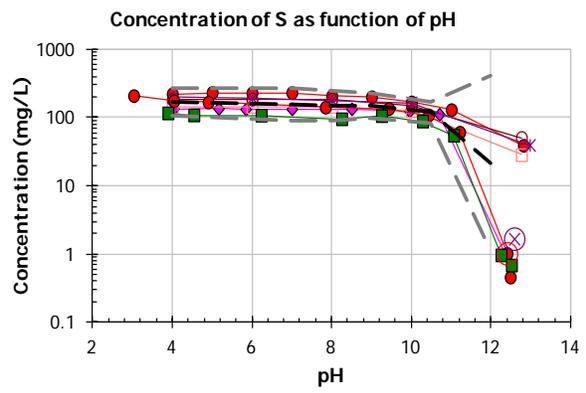
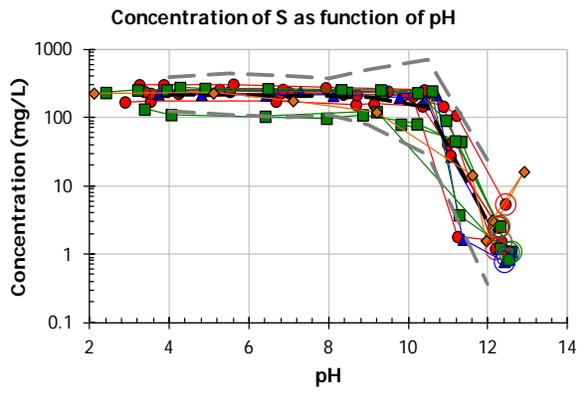
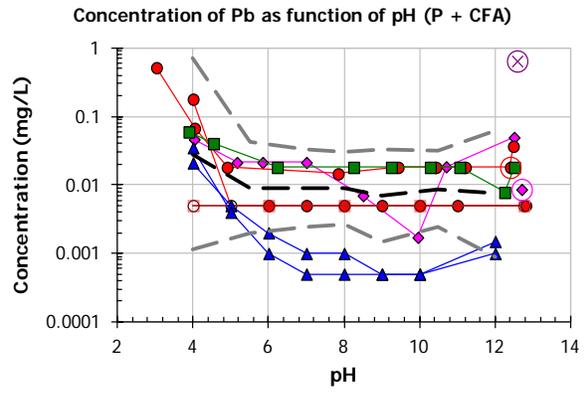
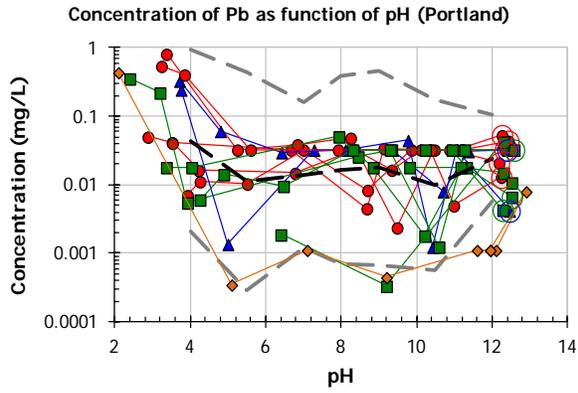
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



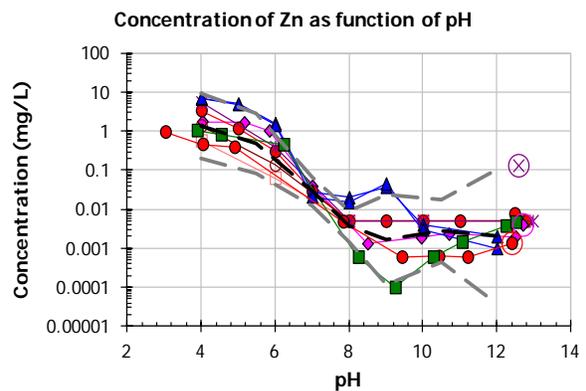
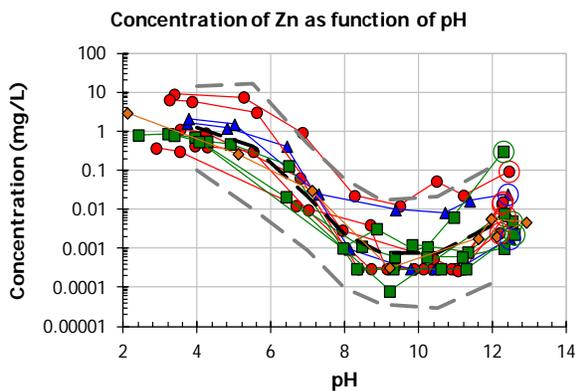
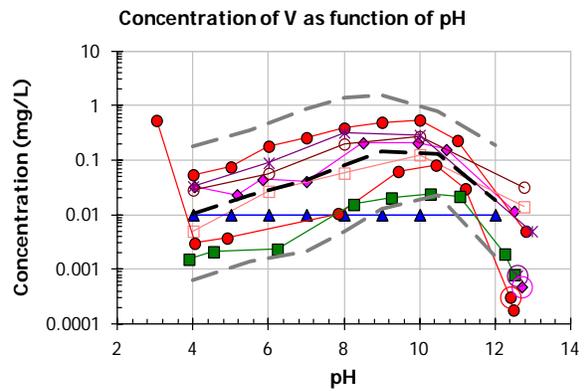
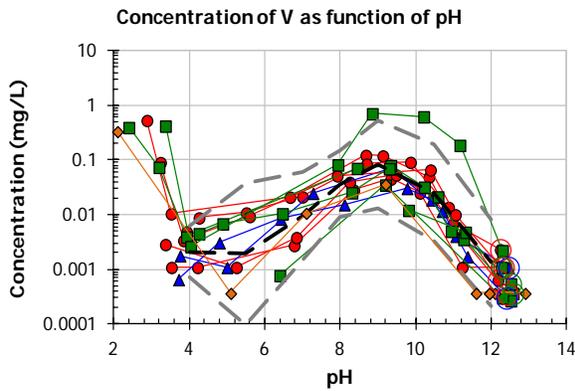
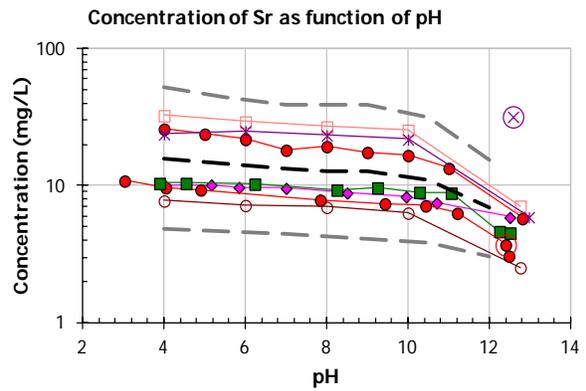
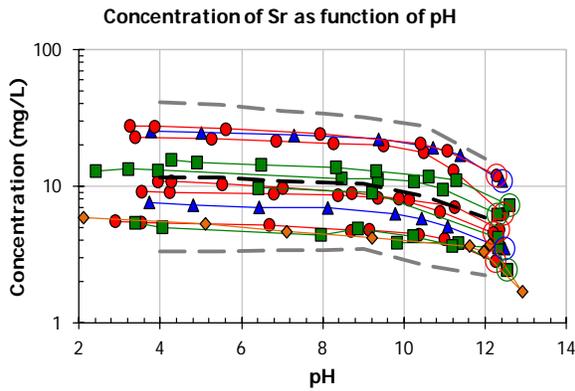
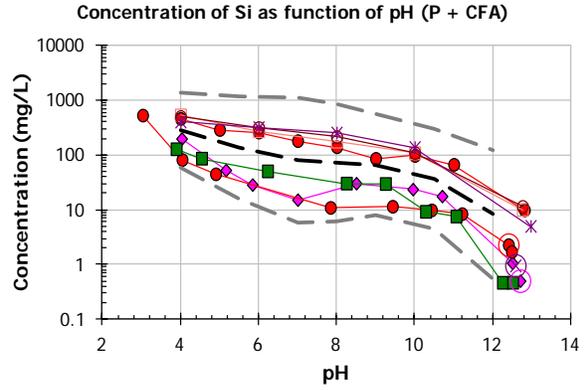
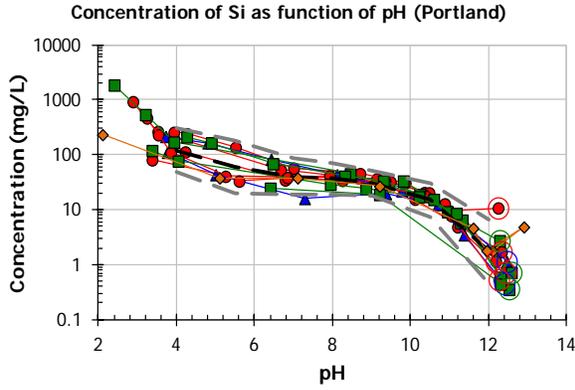
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes



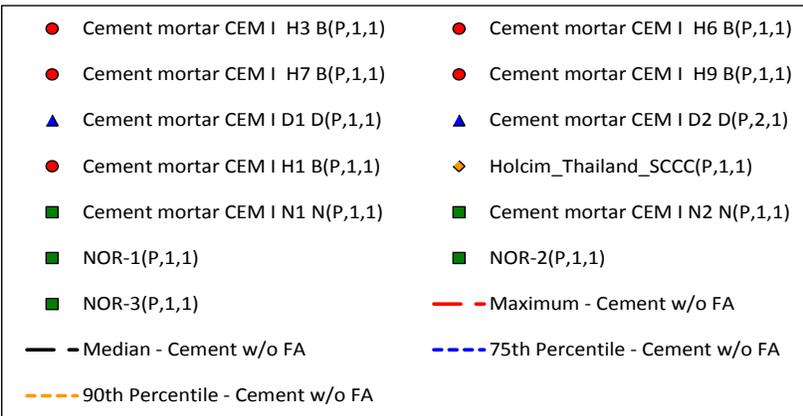
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



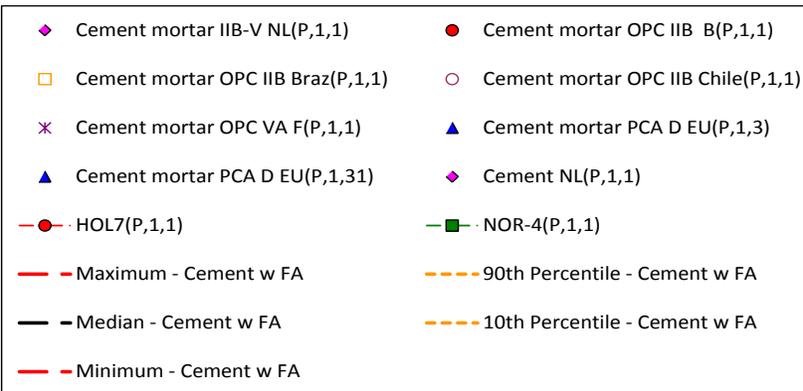
## Appendix B. Comparisons of Leaching Results and Statistics (i.e., Median and Maximum Values) for pH-Dependent Leaching from Cements and Concretes with and without Fly Ash

Legend:

### Cements without Fly Ash



### Cements with Fly Ash



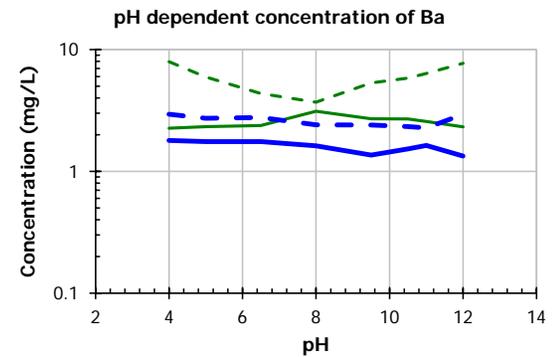
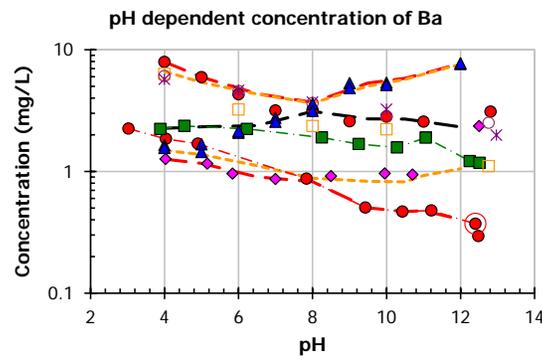
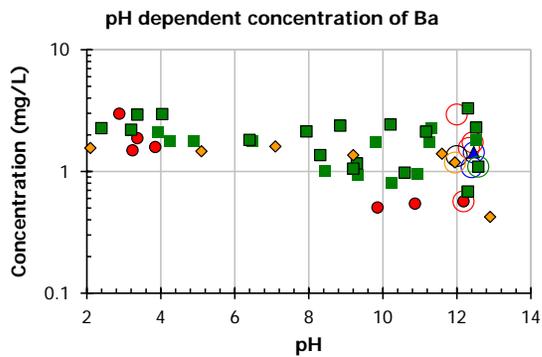
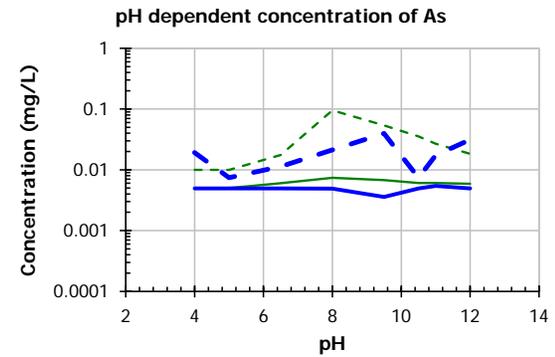
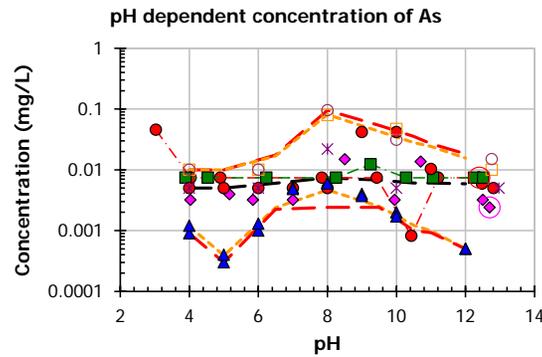
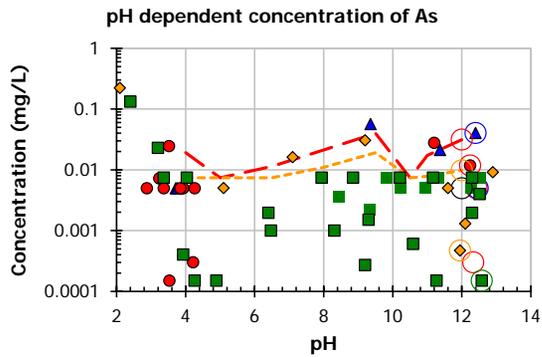
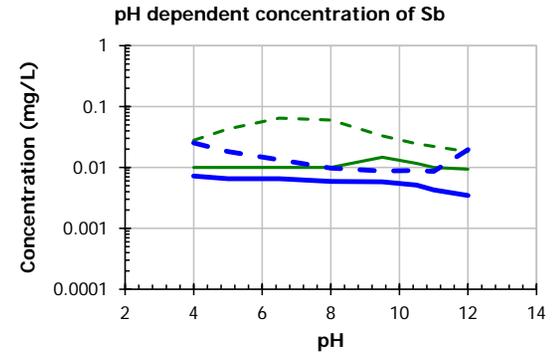
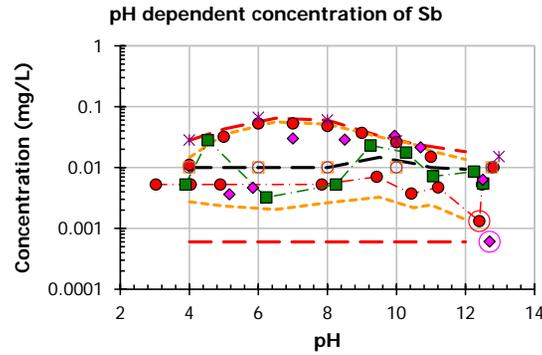
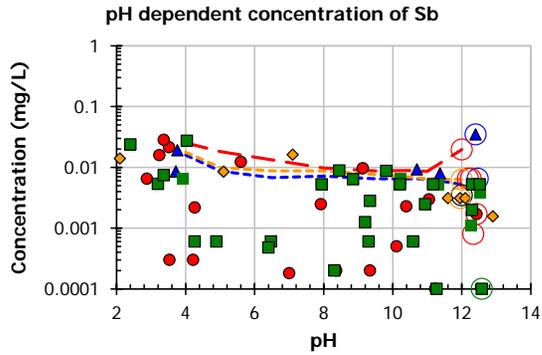
### Median and Maximum



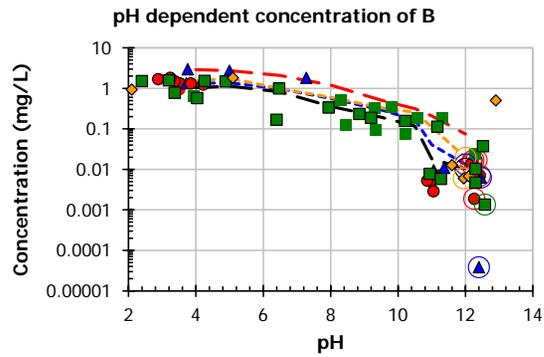
**Cements without Fly Ash**

**Cements with Fly Ash**

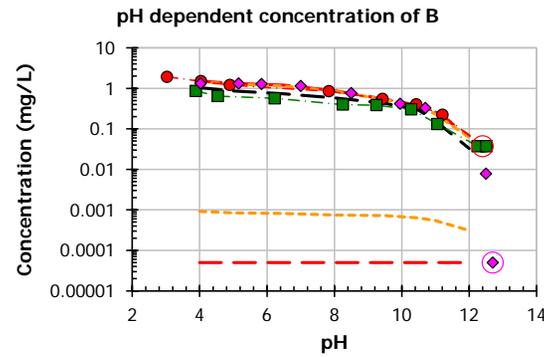
**Median and Maximum**



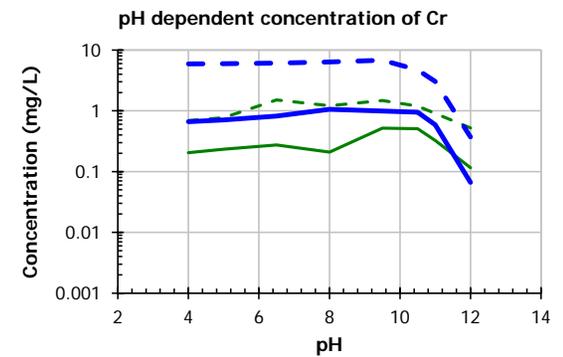
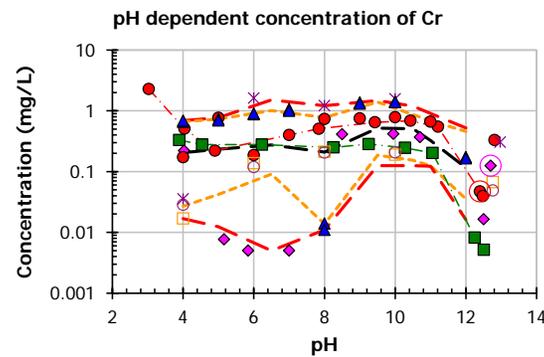
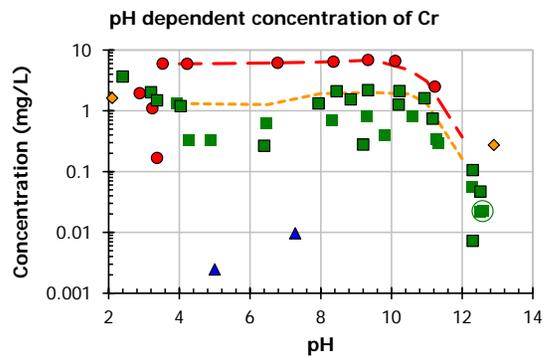
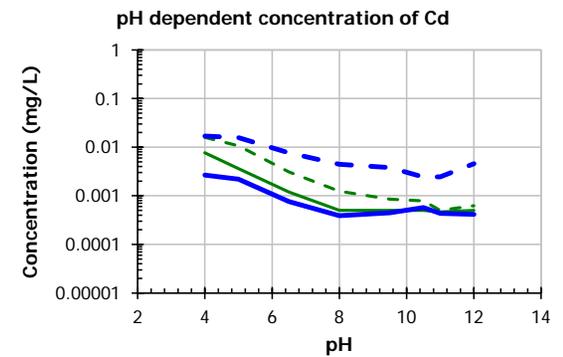
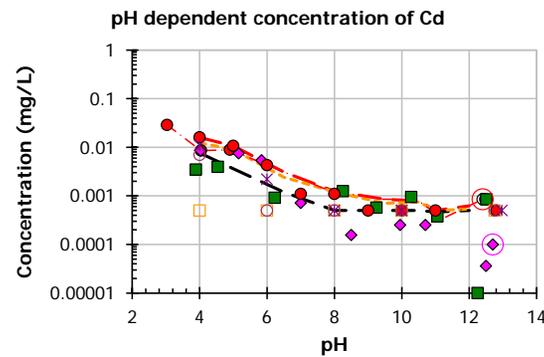
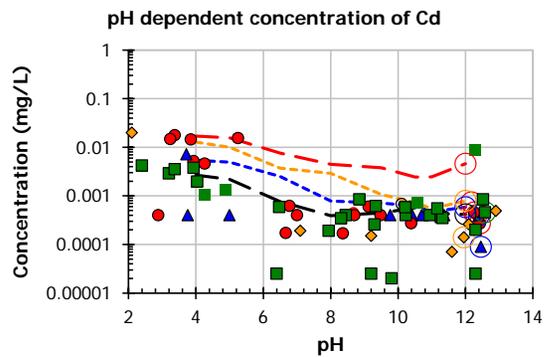
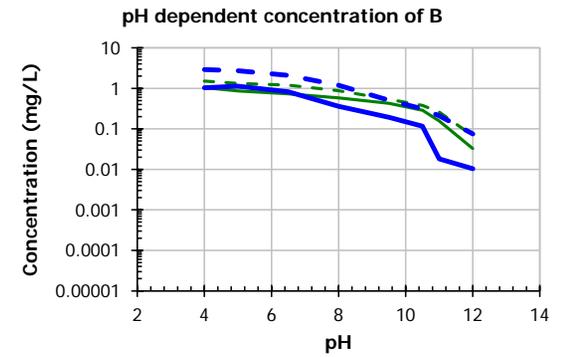
**Cements without Fly Ash**



**Cements with Fly Ash**



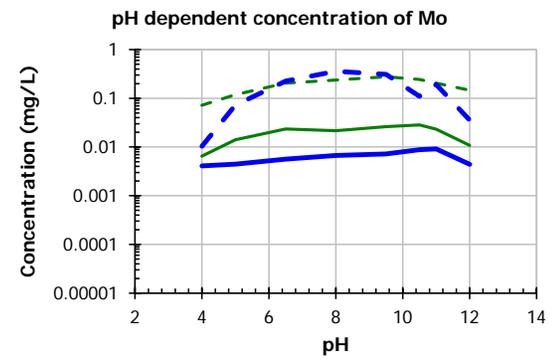
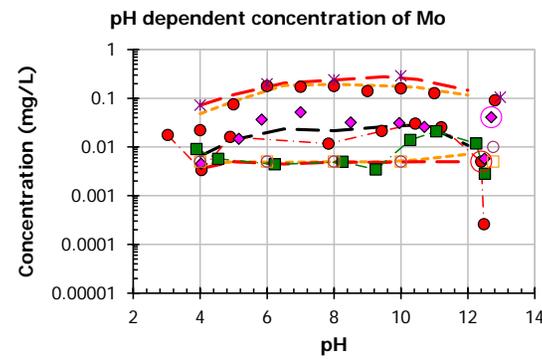
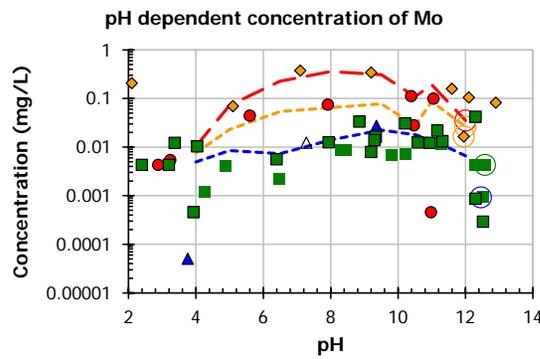
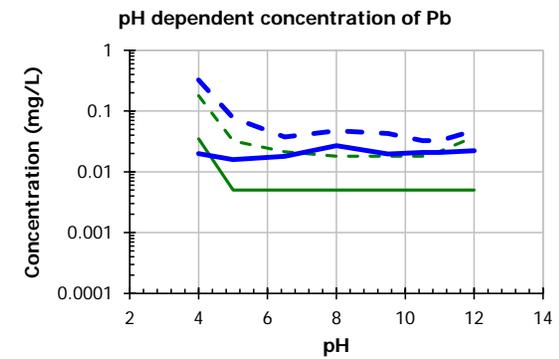
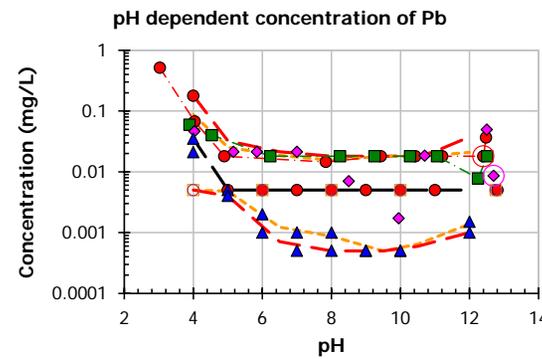
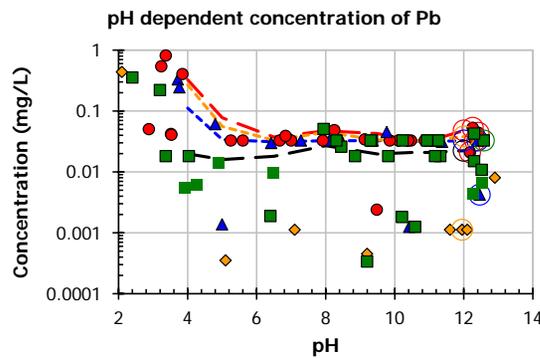
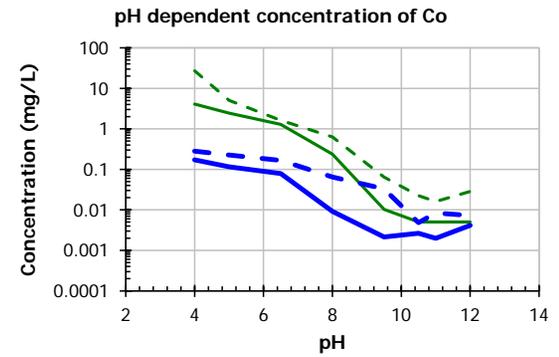
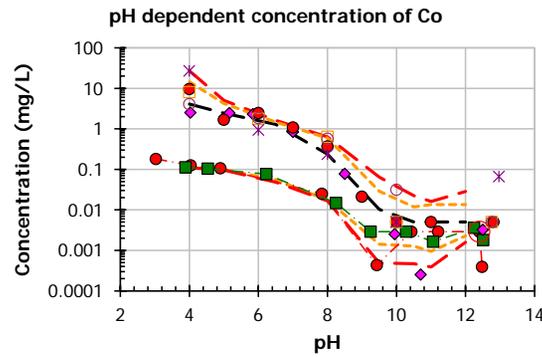
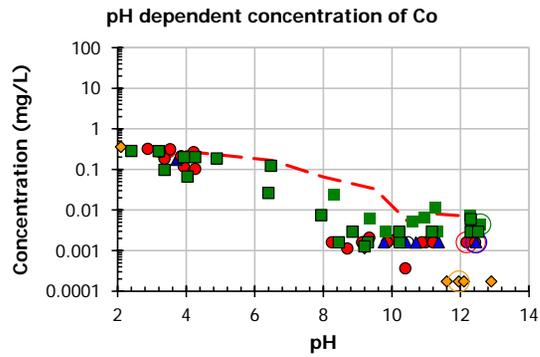
**Median and Maximum**



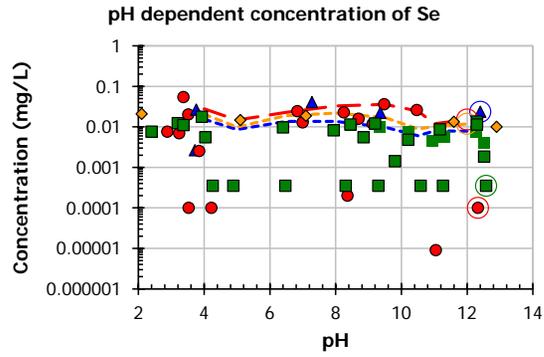
**Cements without Fly Ash**

**Cements with Fly Ash**

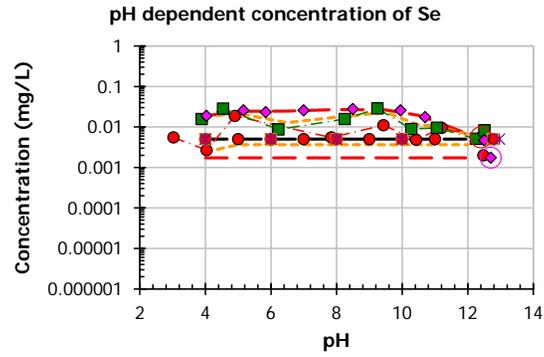
**Median and Maximum**



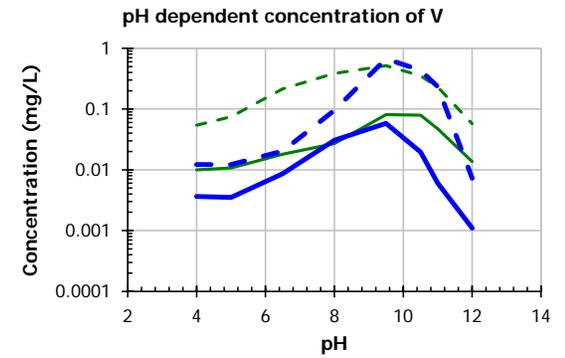
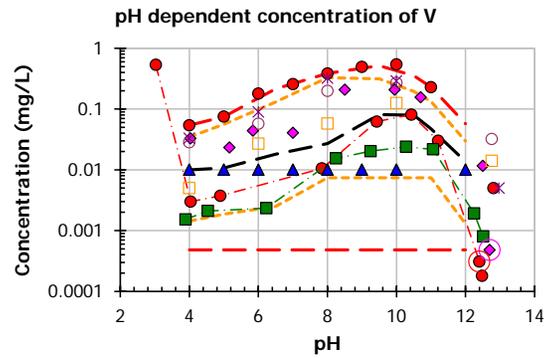
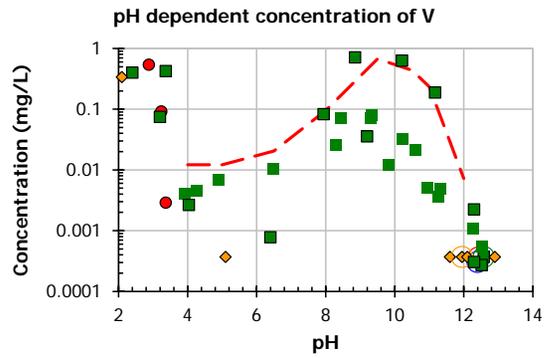
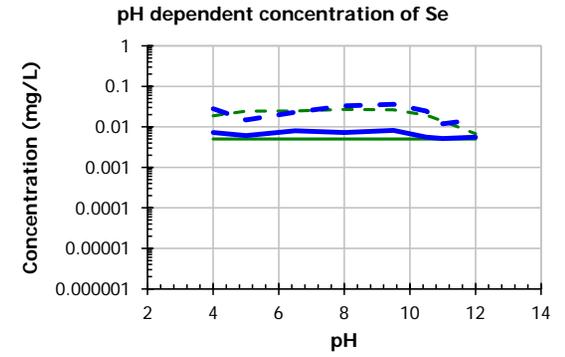
**Cements without Fly Ash**



**Cements with Fly Ash**



**Median and Maximum**



### **Appendix C. Cumulative Release from Monolith Leaching of EU Mortars and Concretes: CEM I (without fly ash) and CEM II/B-V (with fly ash)**

Notes:

- Black horizontal solid lines represent cumulative release leaching criteria from the Dutch Soil Quality Decree.
- Aqua colored symbols indicate carbonated samples to simulate accelerated aging.
- Gray symbols indicate concrete samples.
- Gray dashed lines indicate 90 percent confidence intervals; black dashed lines indicate mean values of the data sets shown.

Legend:

<b>Sample name</b>	<b>Country</b>	<b>Description</b>	<b>Reference</b>
<b>Portland</b>			
Cement mortar CEM I B3	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B7	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D2	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N1	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D1	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B1	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B6	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B9	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N2	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N5s	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM I N5 Carb	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup> Carbonated high CO <sub>2</sub> prior to leaching	van der Sloot et al., 2011
Cement mortar CEM I B6s	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D1s	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

<b>Sample name</b>	<b>Country</b>	<b>Description</b>	<b>Reference</b>
<b>Portland</b>			
Cement mortar CEM I B1s	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N2s	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I D2s	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B3s	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I B7s	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N1s	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot and Hoede, 1997 and van der Sloot, 2000
Cement mortar CEM I N5	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM I TH1	Thailand	QC of cement by testing cement mortar	ECN, 2009
<b>Blended cements and concretes with coal fly ash</b>			
Cement mortar CEM IIB D4	Germany	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM IIB B7	Belgium	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM IIB N4	Norway	Cement mortar according to EN196-1 (W/C=0.5) <sup>1</sup>	van der Sloot et al., 2011
Cement mortar CEM IIB NL 1	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 2	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 3	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 4	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 5	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 6	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 7	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 8	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 9	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Cement mortar CEM IIB NL 10	Netherlands	Cement mortar with 20% cement replacement <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 10	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash	ECN, 2001

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

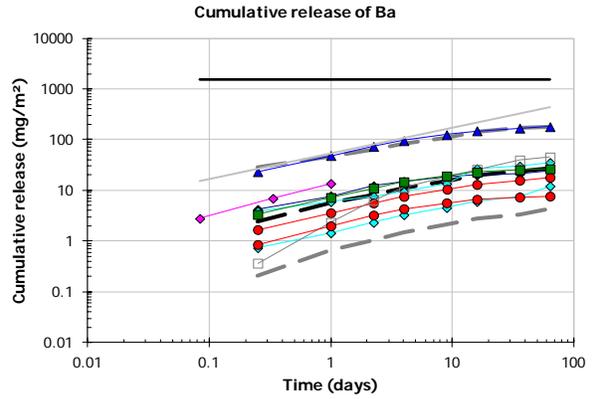
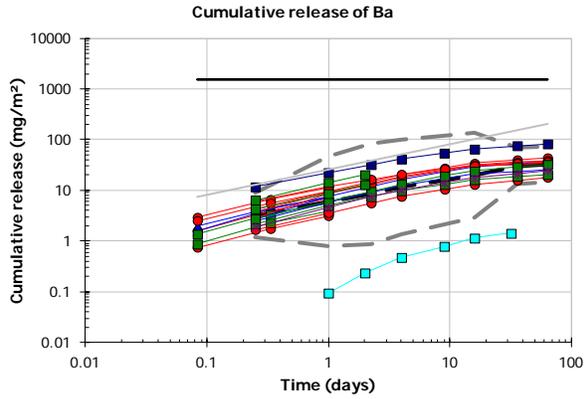
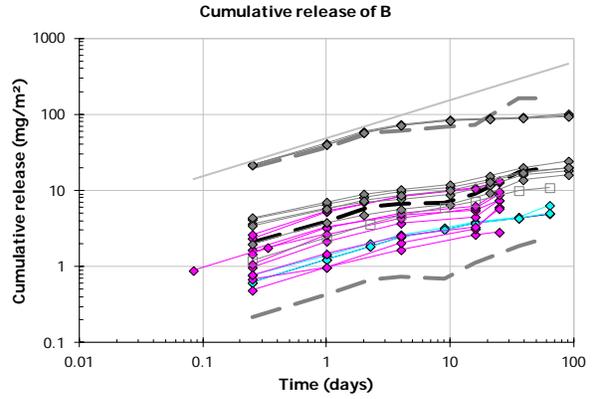
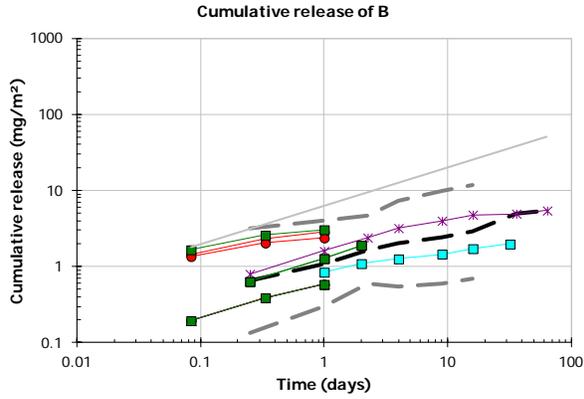
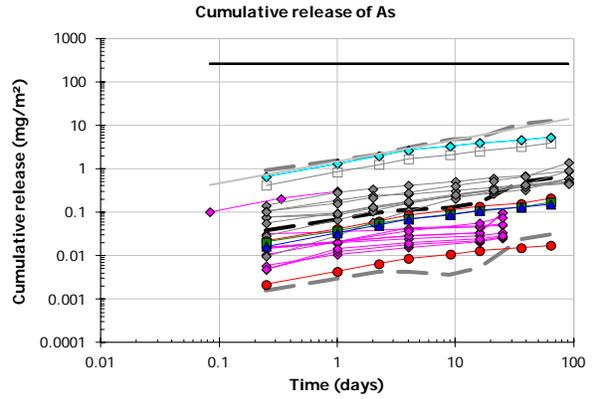
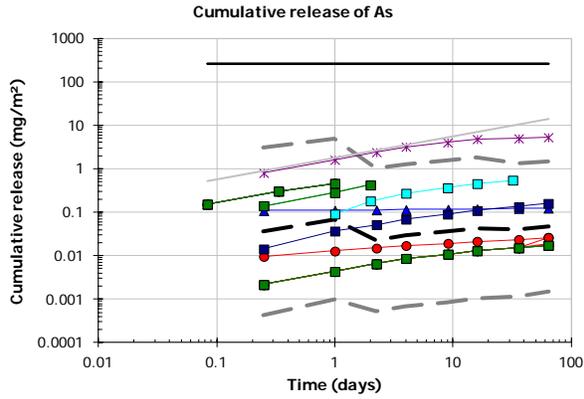
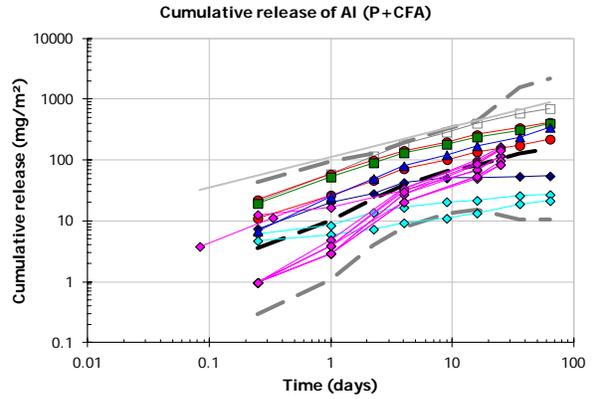
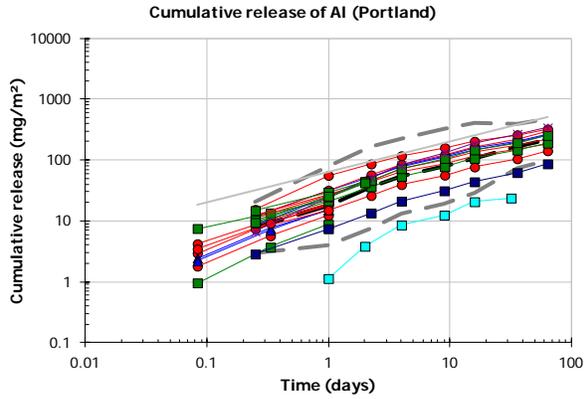
<b>Sample name</b>	<b>Country</b>	<b>Description</b>	<b>Reference</b>
<b>Blended cements and concretes with coal fly ash</b>			
Concrete CEM IIB NL 10 Carb2	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. Carbonated prior to testing	ECN, 2001
Concrete CEM IIB NL 10 Carb3	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. Carbonated prior to testing	ECN, 2001
Concrete CEM IIB NL 1	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 2	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 3	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 4	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 5	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 6	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 7	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 8	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 9	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985
Concrete CEM IIB NL 11	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	van der Sloot et al., 1998
Concrete CEM IIB NL 12	Netherlands	Concrete cube with 20 % cement replacement by coal fly ash. <sup>2</sup>	Van der Sloot and Weyers, 1987 and van der Sloot et al., 1985

Notes:

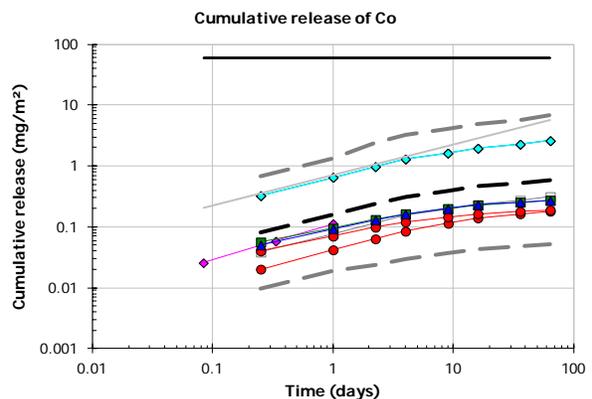
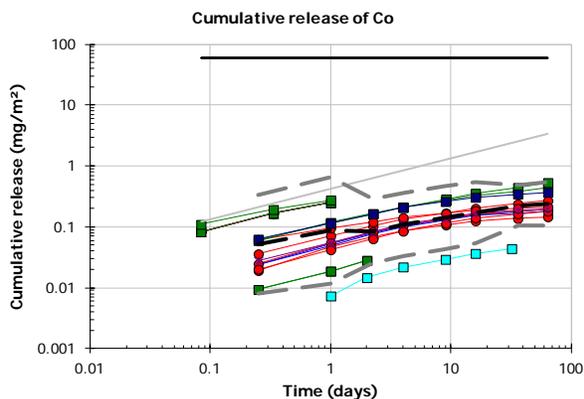
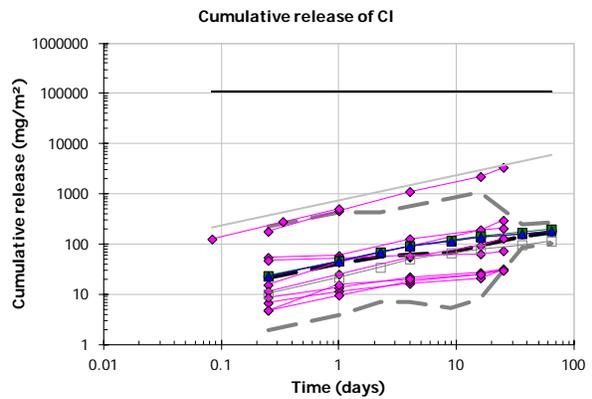
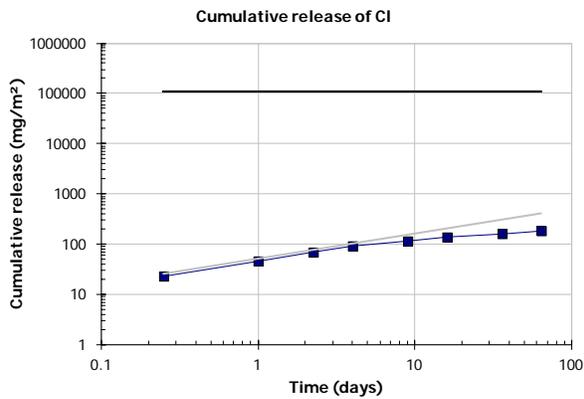
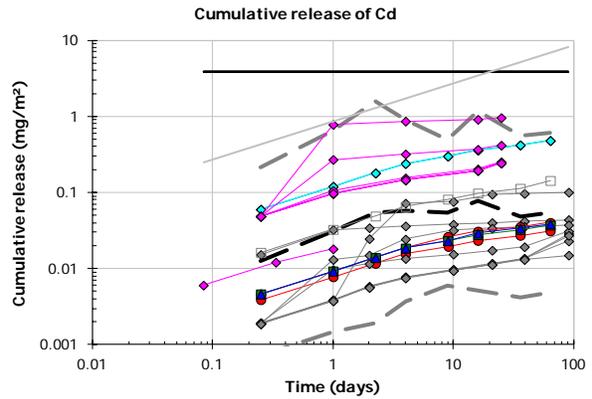
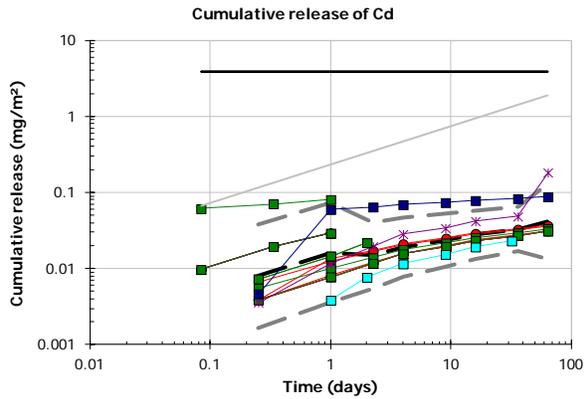
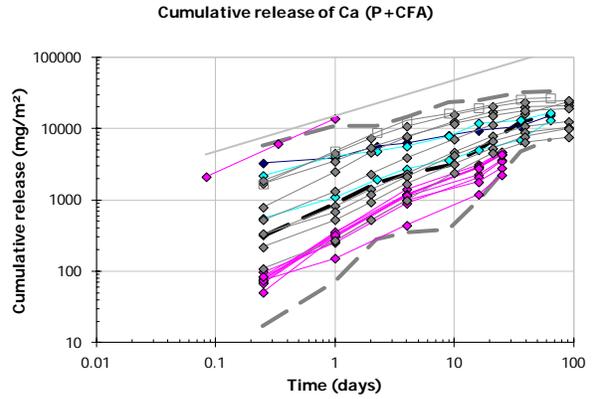
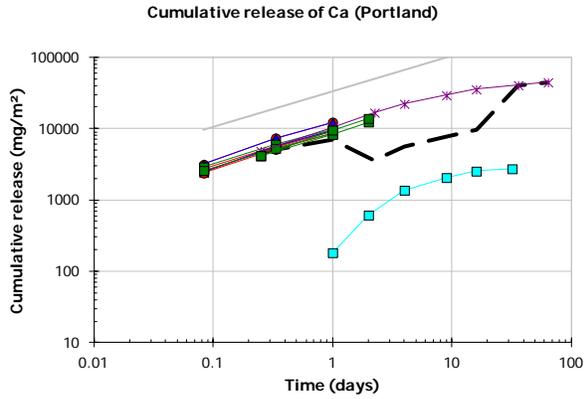
<sup>1</sup> After de-molding at the age of 24 hours, the mortar samples for the leaching tests were cured at 20 °C and 95 % relative humidity for another 27 days in plastic bags to prevent pre-leaching

<sup>2</sup> Number denotes different fly ash resulting from processing coal from worldwide sources in Dutch coal fired power plants.

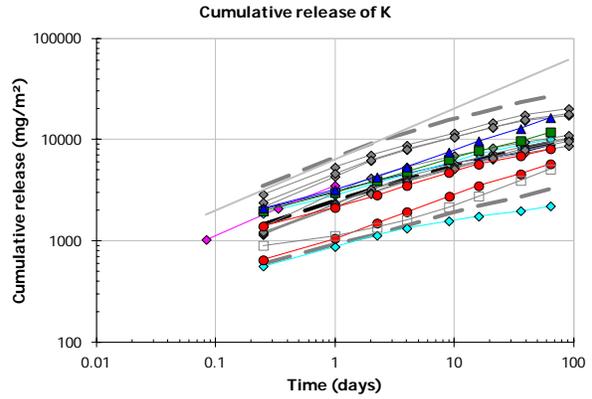
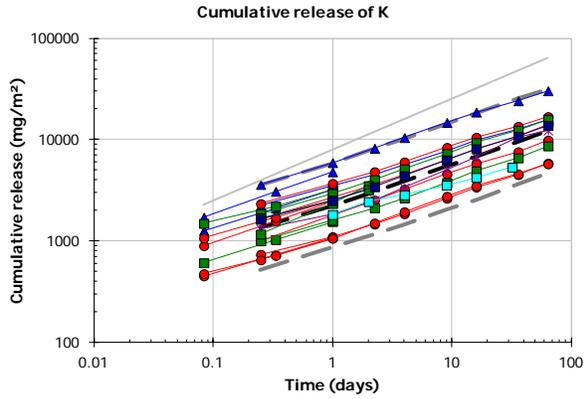
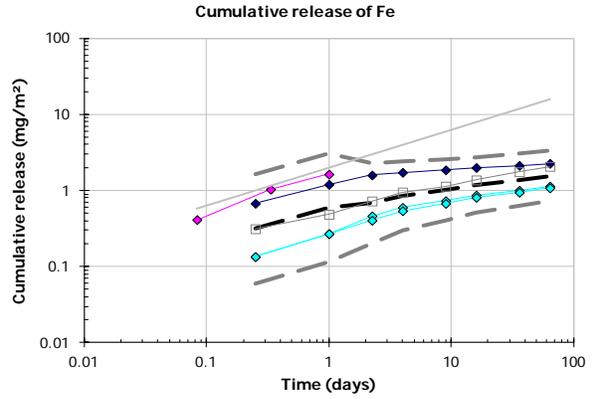
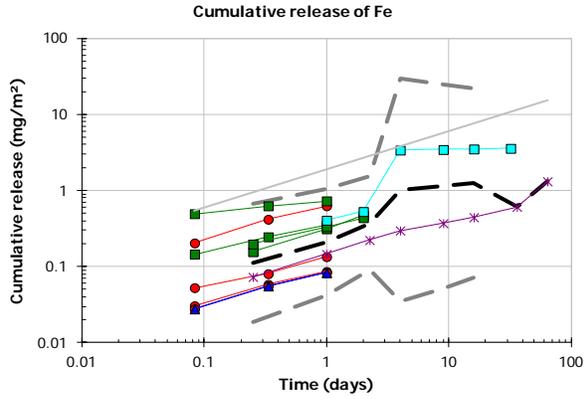
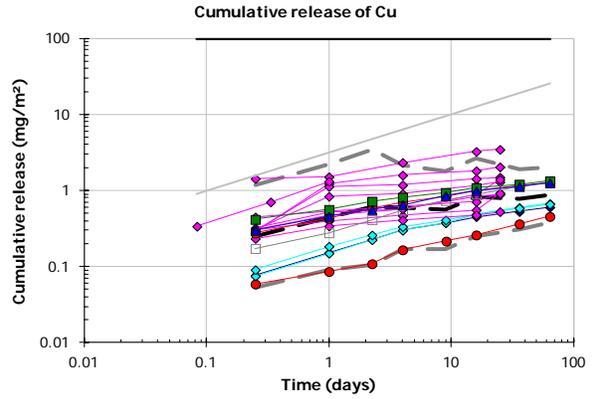
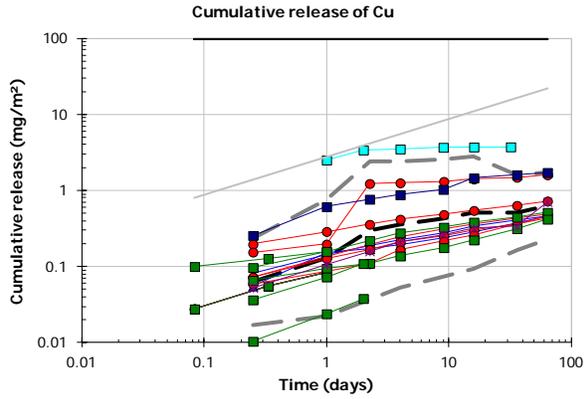
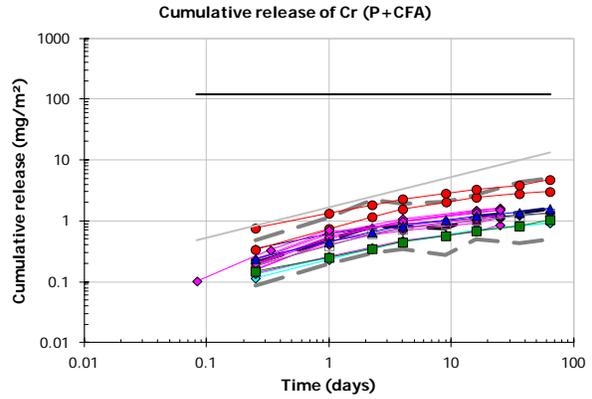
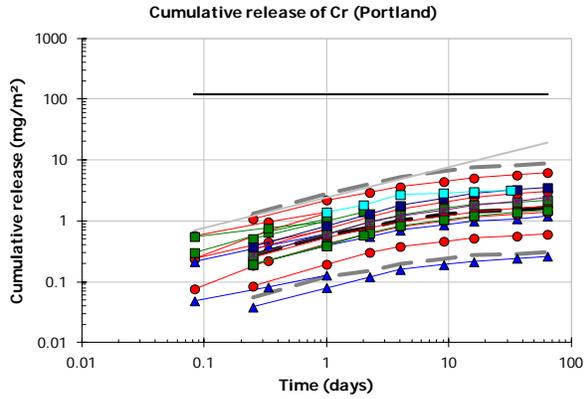
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



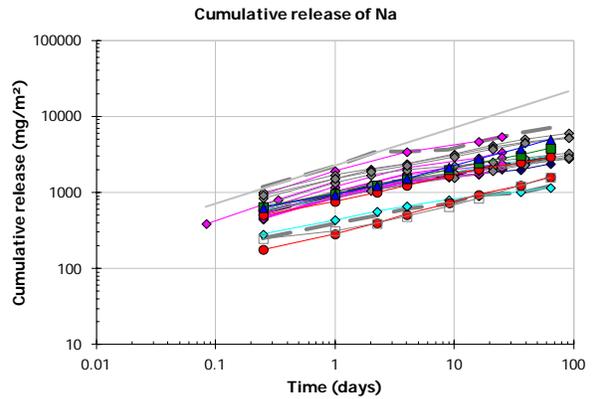
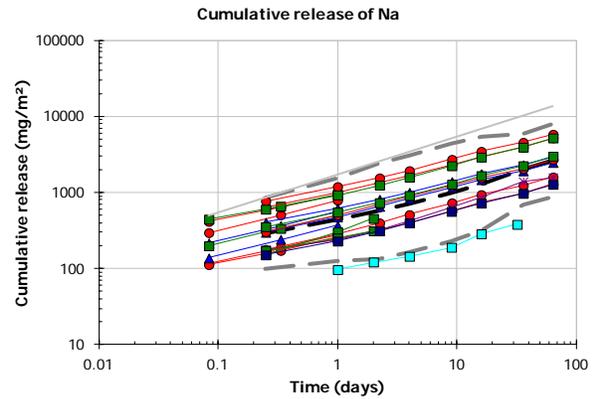
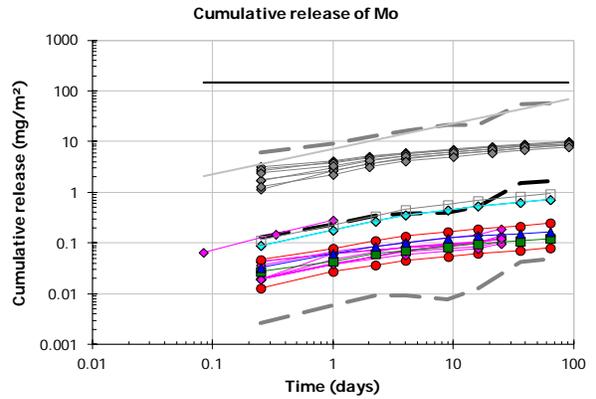
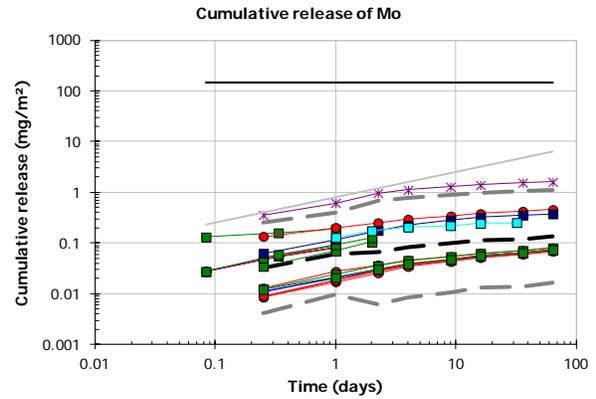
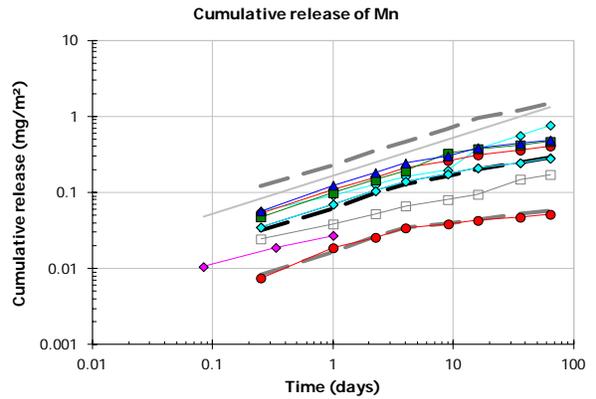
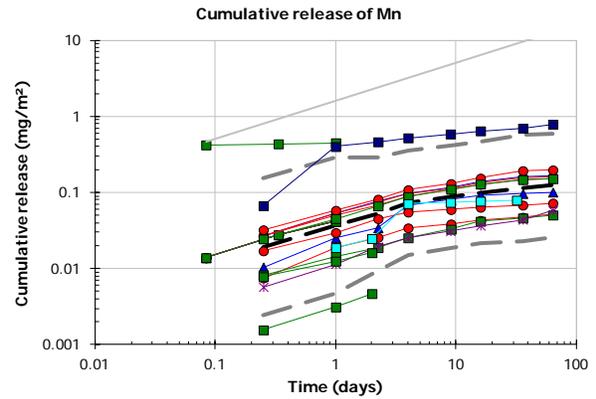
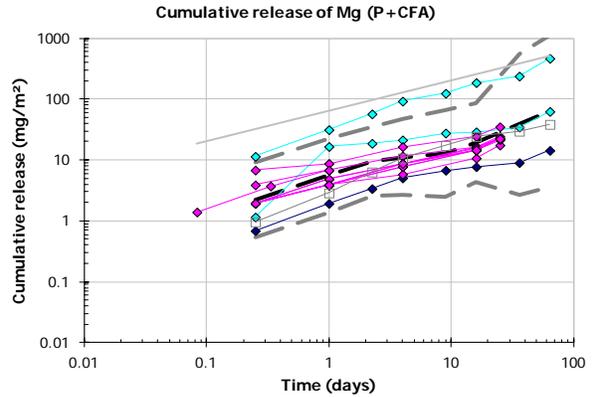
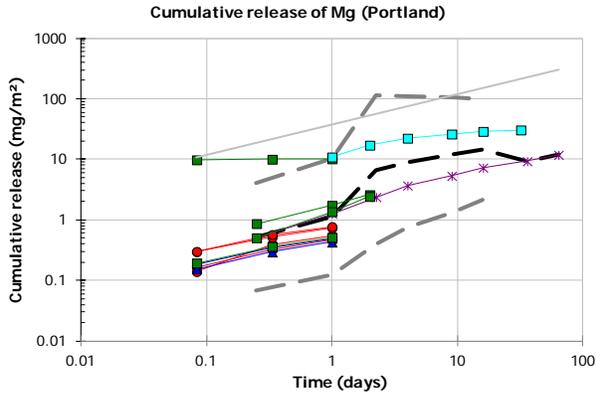
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



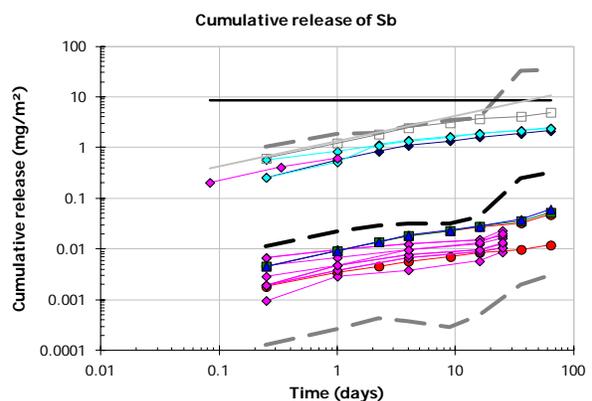
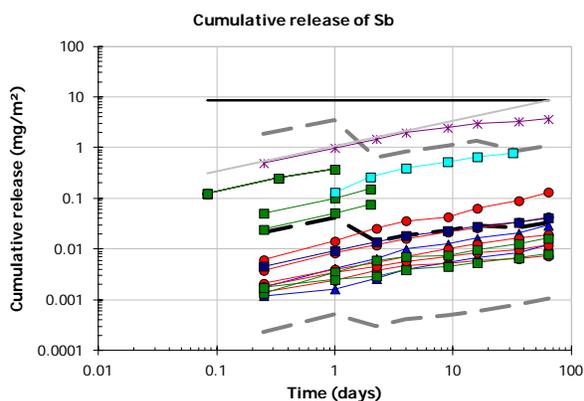
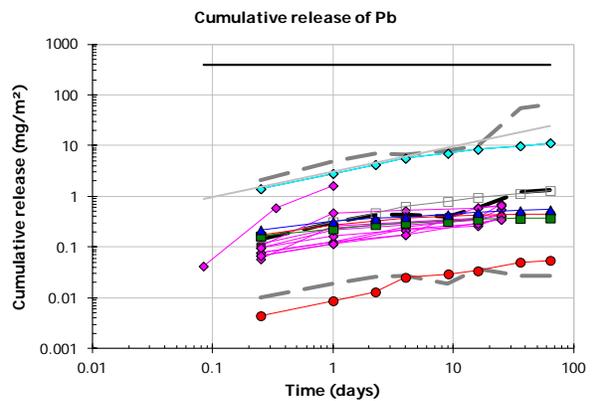
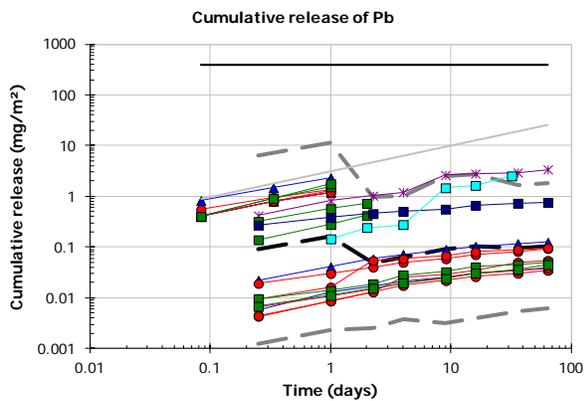
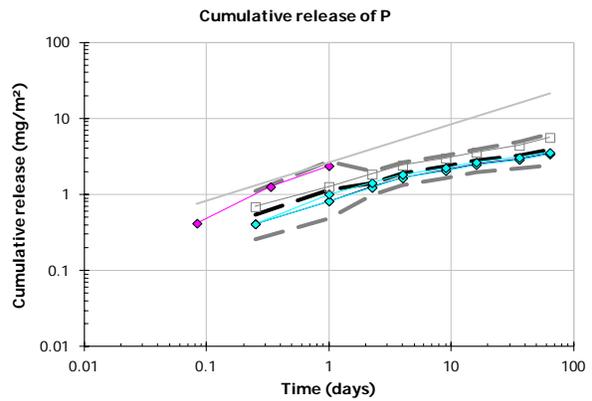
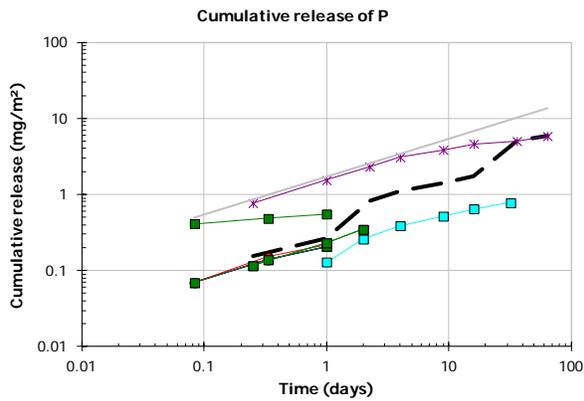
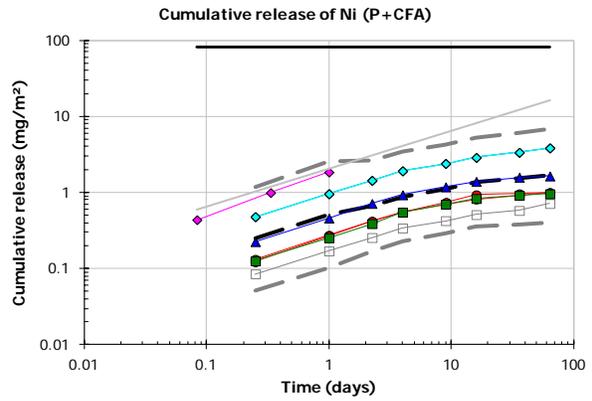
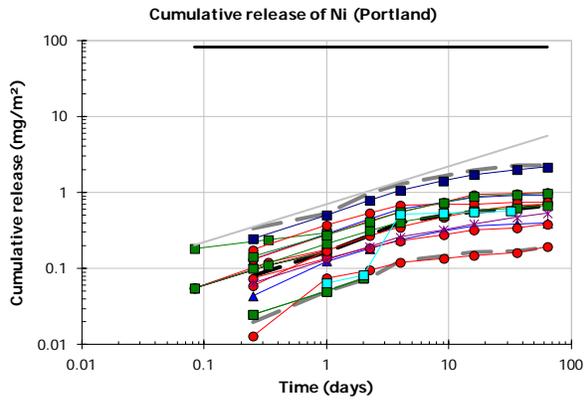
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



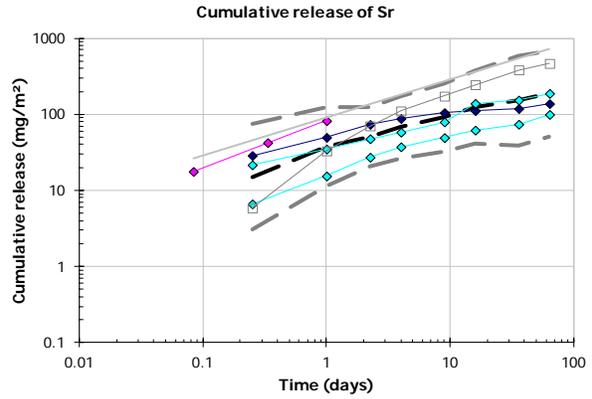
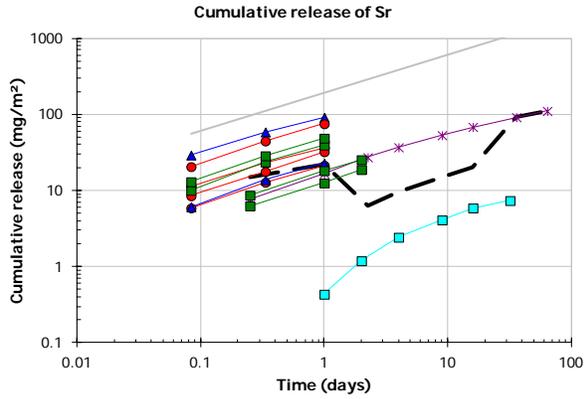
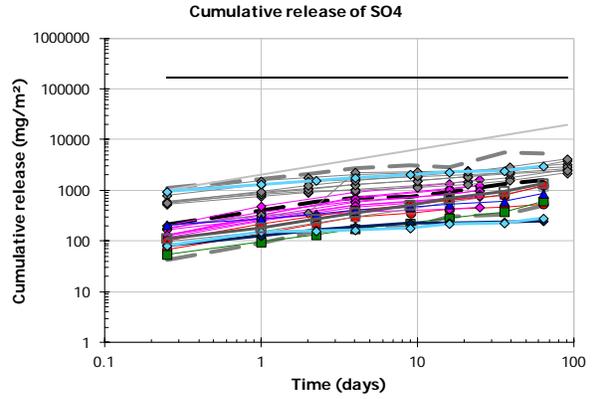
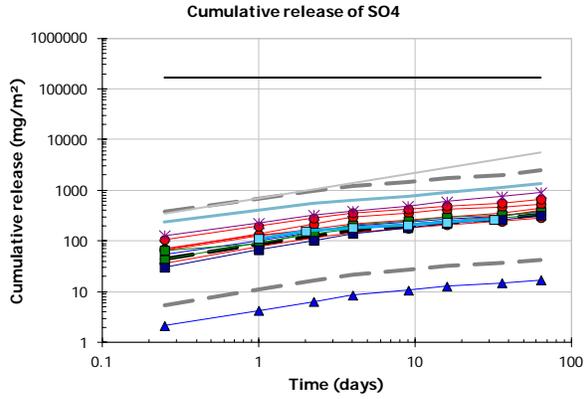
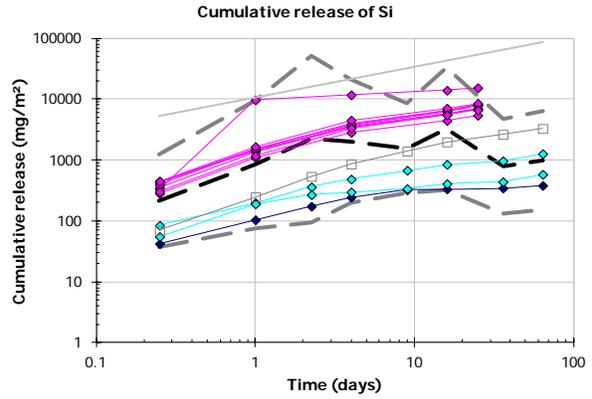
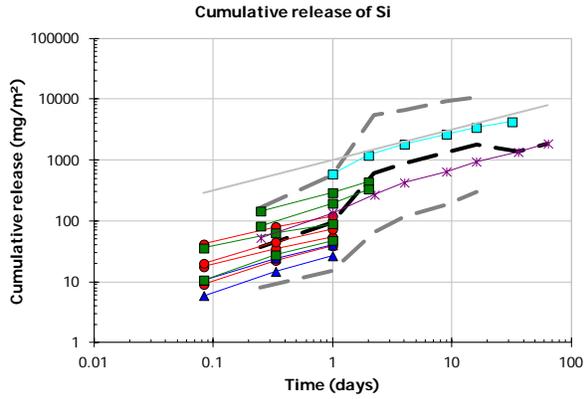
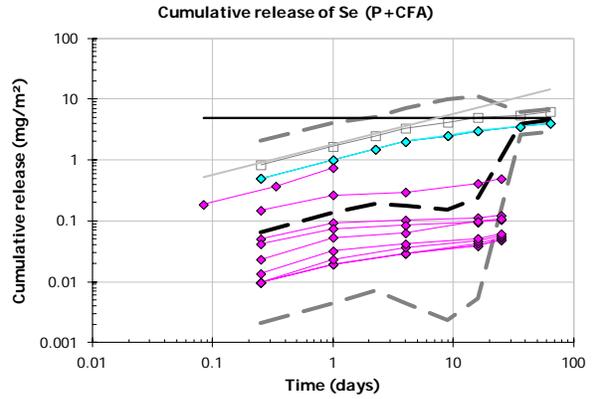
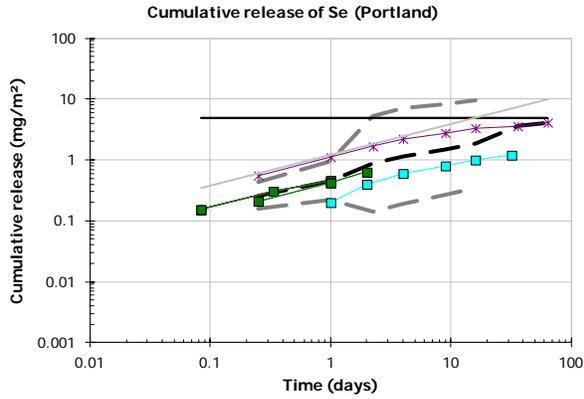
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



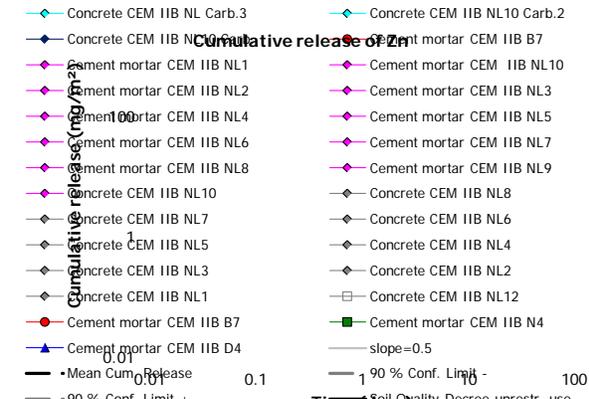
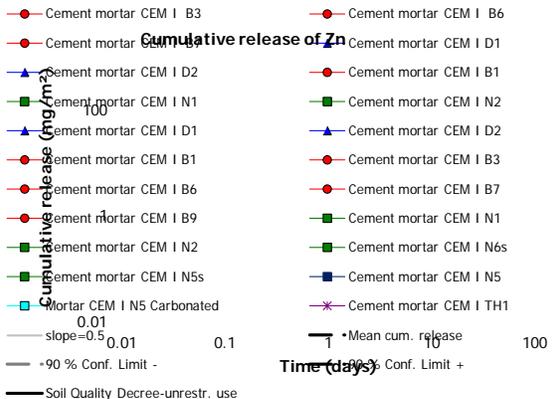
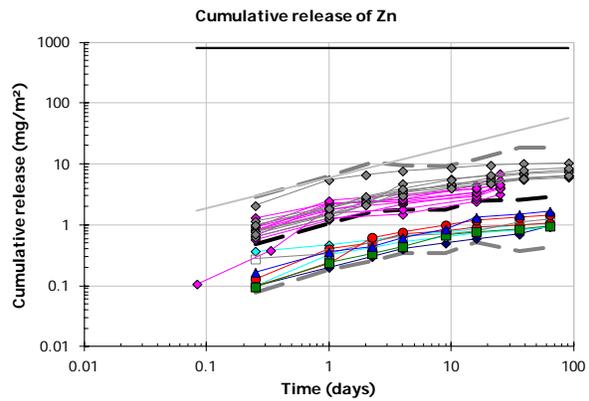
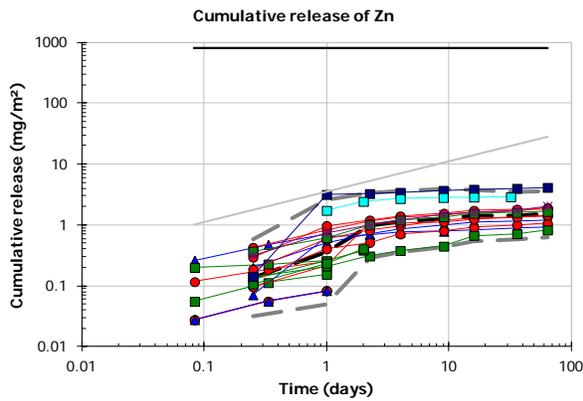
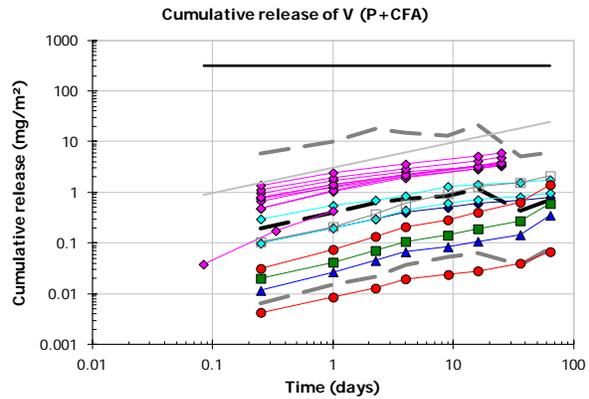
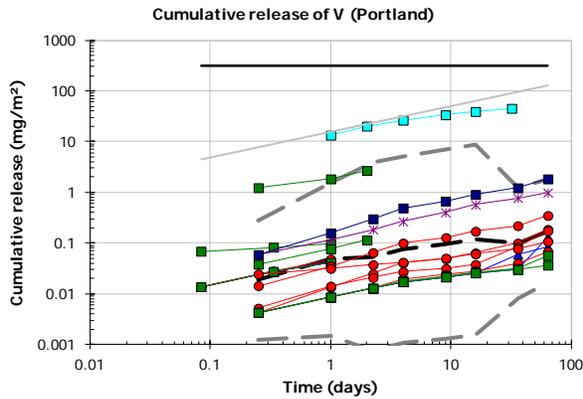
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



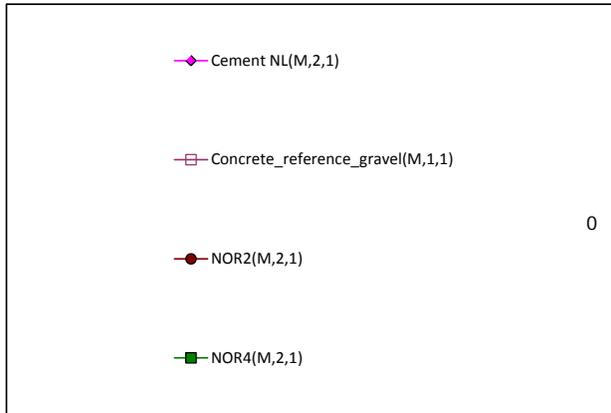
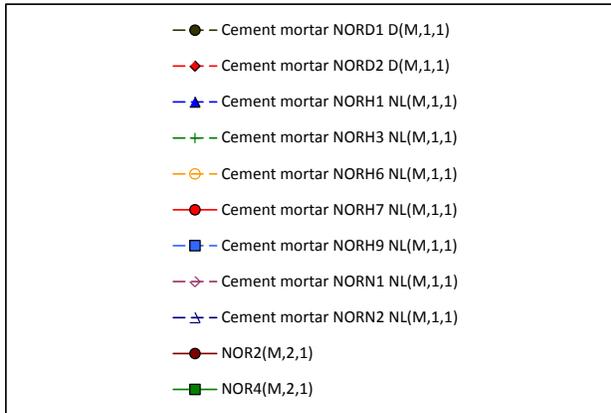
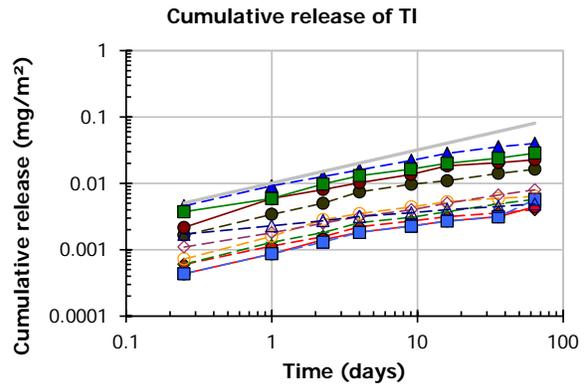
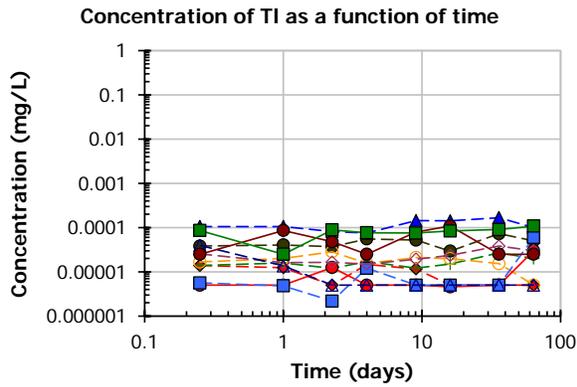
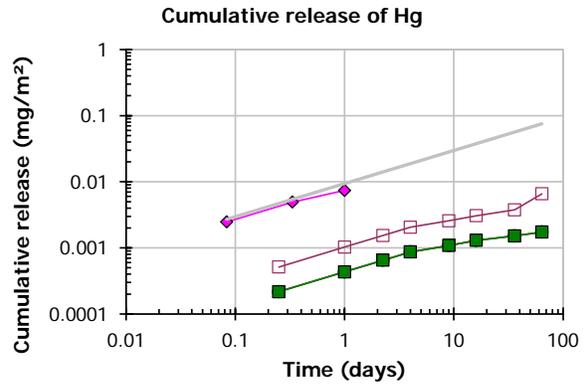
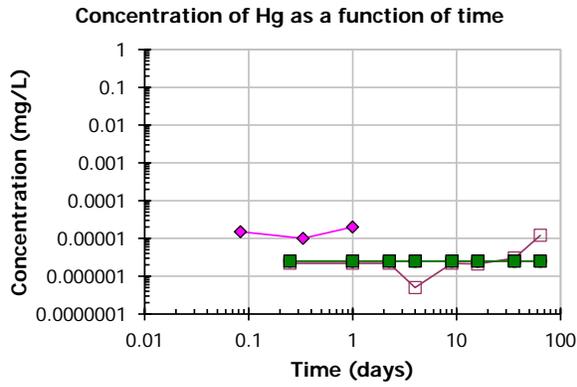
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



# The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes



The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes



### **Appendix D. Approach for Criteria Development for Monolithic Materials in the Dutch Soil Quality Decree (2007)**

From 1995-2008, the Dutch Building Materials Decree (BMD) has regulated the potential impact of construction materials on the environment. The decree specifies the environmental quality criteria for the application of stony materials (including excavated soil) in construction, and does not distinguish between primary, secondary and waste materials. After 10 years of experience with the BMD, a revision of the Decree was found necessary, for reasons of costs and transparency following the publication of several amendments with exemptions.

The aim of the revision, currently the Soil Quality Decree that came into force in July 2008, was to develop a simplified and more transparent regulation containing a consistent set of emission limit values, which warrant the protection of soil and groundwater quality with minimal restrictions for the re-use of (secondary) materials.

In the derivation of emission limits for inorganic substances, maximum permissible concentrations (MPCs) have been used as the environmental quality criteria (compliance values). At the MPC level, ecosystems are not significantly affected by chemical exposure. For inorganic substances occurring at natural background concentrations, the MPC is transformed to a corresponding maximum permissible addition (MPA), using  $MPC = MPA + \text{background}$  (see Verschoor et al., 2008, and references therein). The MPA values for the regulated inorganic substances are listed in Table C-1. No MPA values are available for Cl, Br, F and SO<sub>4</sub> in soil and, as a consequence, emission limit values for these substances are solely based on their effect on groundwater.

**Table D-1 Maximum permissible addition value for soil (MPA<sub>s</sub>) and groundwater (MPA<sub>g</sub>) used in the derivation of emission limits for granular construction products in the Dutch Soil Quality Decree.**

Component	Symbol	MPA <sub>s</sub> (mg/kg)	MPA <sub>g</sub> (µg/L)	Component	Symbol	MPA <sub>s</sub> (mg/kg)	MPA <sub>g</sub> (µg/l)
Antimony	Sb	0.53	6.2	Nickel	Ni	0.26	1.9
Arsenic	As	0.9	24	Selenium	Se	0.11	5.3
Barium	Ba	180	29	Tin	Sn	34	20
Cadmium	Cd	0.79	0.34	Vanadium	V	1.1	3.5
Chromium	Cr	0.38	8.7	Zinc	Zn	16	7.3
Cobalt	Co	2.4	2.6	Bromide	Br	<i>n.a.</i>	8,000
Copper	Cu	3.4	1.1	Chloride	Cl	<i>n.a.</i>	200,000
Mercury	Hg	1.9	0.23	Fluoride	F	<i>n.a.</i>	1,500
Lead	Pb	55	11	Sulphate	SO <sub>4</sub>	<i>n.a.</i>	100,000
Molybdenum	Mo	39	29				

*n.a.* = not available

An important premise in the criteria development for monolithic products in the Soil Quality Decree is that the release from 1 m<sup>2</sup> of construction products or stabilized monolithic waste impacts on 1 m<sup>2</sup> of soil surface. Through this assumption the real surface area of a construction product impacting on soil is not taken into consideration. This simplification is used to ensure a straightforward approach without diversification in multiple sizes and shapes found in reality.

The release from construction products is derived from the test results in the laboratory test (Tank leach test) in the following manner:

$$I_{soil} = E_{ave,64d} \cdot f_{extrap} \cdot f_{temp}$$

where  $I_{soil}$  is the release to soil from a monolithic product expressed in mg/m<sup>2</sup> over  $J$  years,

$E_{ave,64d}$  is the release from monolith leach test in mg/m<sup>2</sup>,

$f_{extrap}$  is the factor of extrapolating release from 64 days to  $J$  years taking into account thickness (m), wet/dry periods, and effective diffusion coefficient ( $D_e$ ), and

$f_{temp}$  is the correction factor for temperature difference between laboratory (20 °C) and field conditions. Taking an average temperature of 10 °C in the Netherlands results in a factor of about 0.7 (Aalbers et al., 1993).

The extrapolation factor for release in 64 days to  $J$  years had been established in the Building Materials Decree (1995) by Aalbers et al (1993). The factor considers the thickness of the product and wetting/drying cycles of exposed products by considering the times that a product is wet due to exposure to rain (% of time wet). The extrapolation factor also considers the effective diffusion coefficient (substance dependent). Thus, thick products that have a high effective diffusion coefficient (worst case condition) require a larger factor than thinner products with a low effective diffusion coefficient. In the Building Materials Decree, default values for various building products have been derived.

For wetting/drying cycles, a distinction is made between permanently wetted products (in ground or surface water), where the correction factor for wetting/drying is 1 (Application type A), and products exposed to rain above ground in which case the correction is factor of 0.1 (assumed for the case of 10% wet time) (Application type B).

- For Application type A, the overall value of  $f_{extrap}$  varies from 1 to 15 depending on the product thickness and the effective diffusion coefficient. In the calculations for the Soil Quality Decree the same parameter settings were used for this application type as for the Building Materials Decree, namely a factor of 15 corresponding with a product thickness of 0.3 m and a  $D_e$  of 10<sup>-10</sup> m<sup>2</sup>/s.
- For Application type B, the overall  $f_{extrap}$  value varies from 1 to 5. In the calculations for the Soil Quality Decree the same parameter settings were used for this application type as for the Building Materials Decree, namely a factor of 5 corresponding with a product thickness of 0.2 m and a  $D_e$  of 10<sup>-10</sup> m<sup>2</sup>/s.

*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

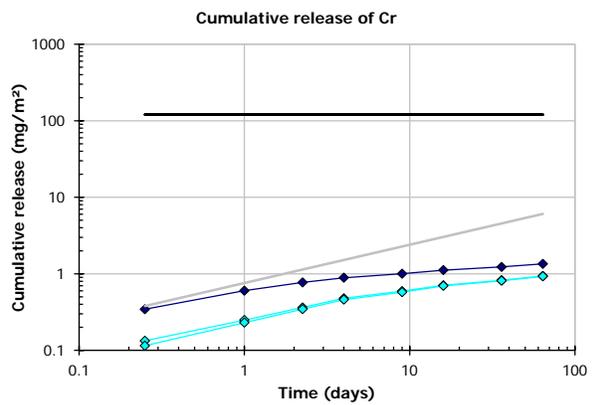
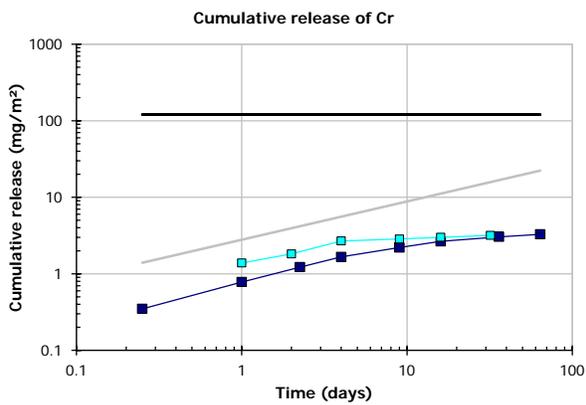
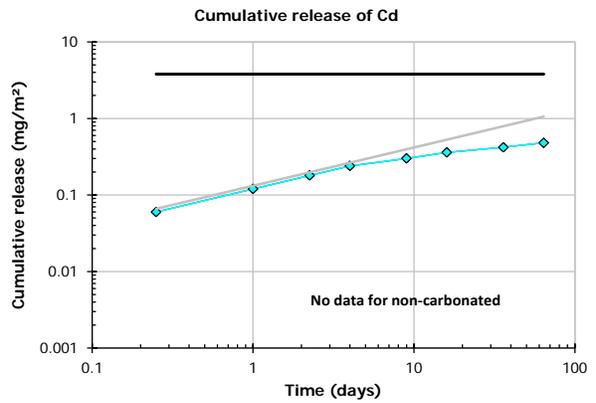
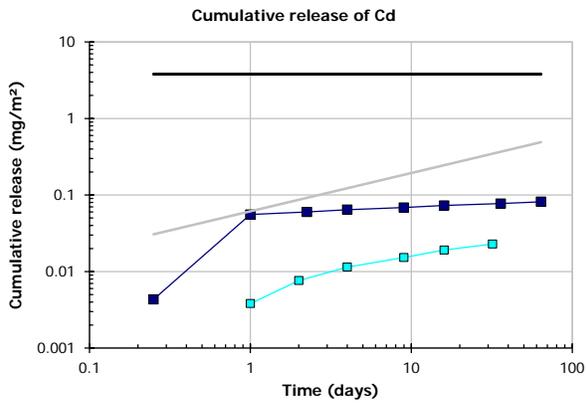
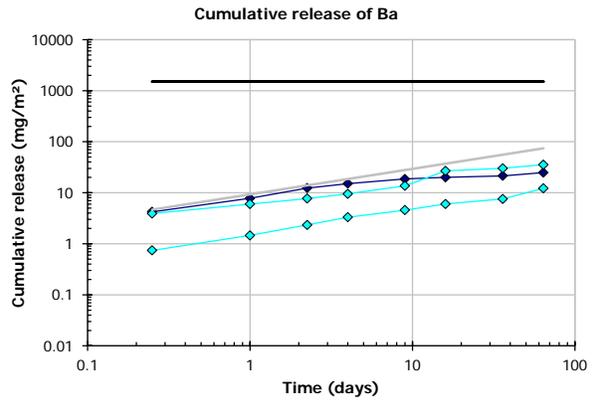
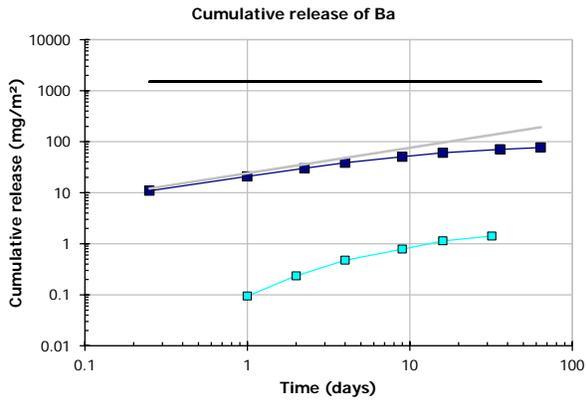
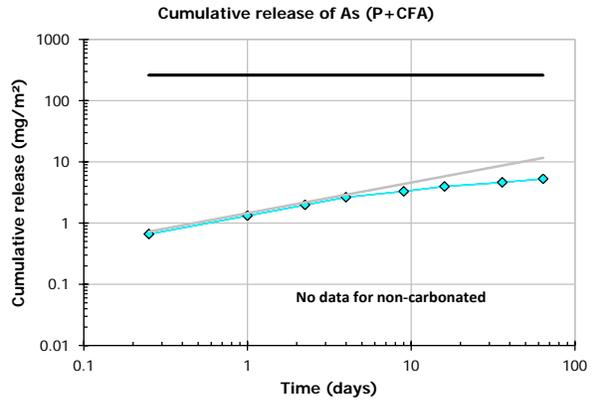
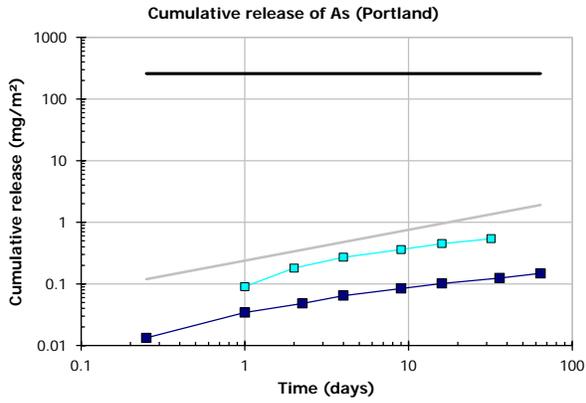
The time dependent release expressed in  $\text{mg}/\text{m}^2$  as a function of time is converted to concentrations by taking the average annual infiltration into account (expressed in  $\text{L}/\text{m}^2$ ) and proportionally divided over a year as needed. The resulting concentration time function is used as input for the chemical reaction transport model, which couples the source term with the concentrations in groundwater at the point of compliance.

**Appendix E. Effect of Carbonation on Monolithic Leaching of EU Cement Mortars:  
CEM I (without fly ash) and CEM II/B-V (with fly ash)**

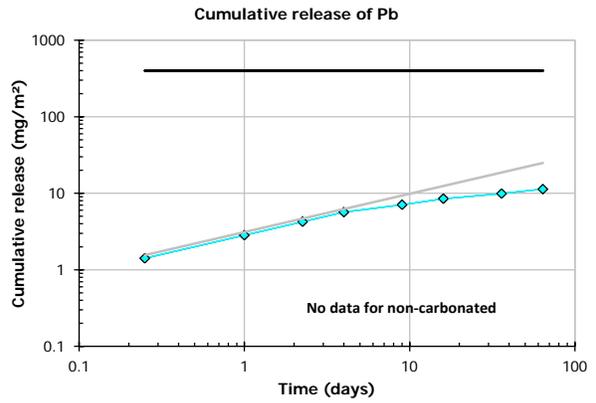
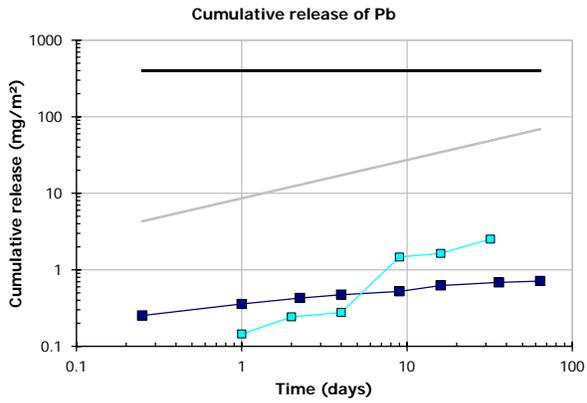
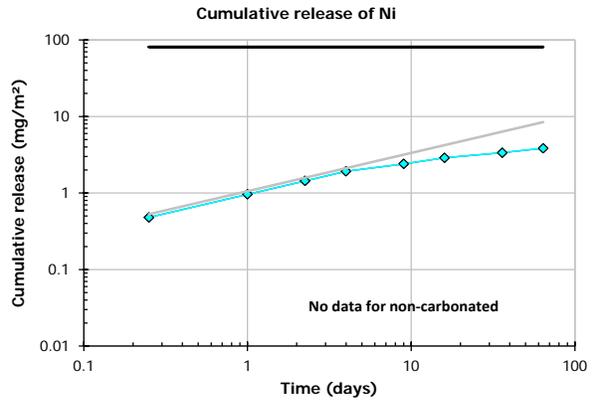
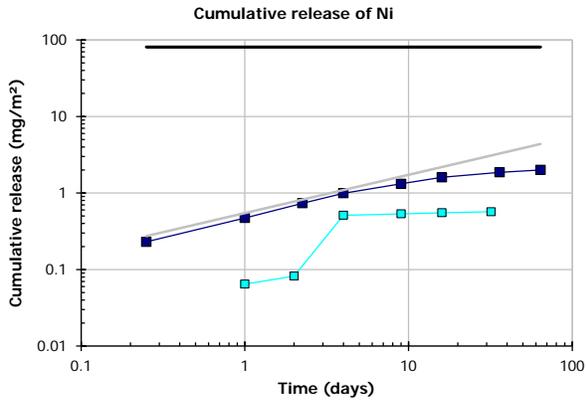
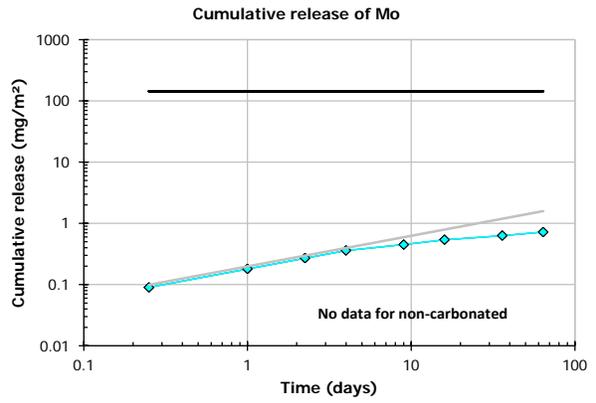
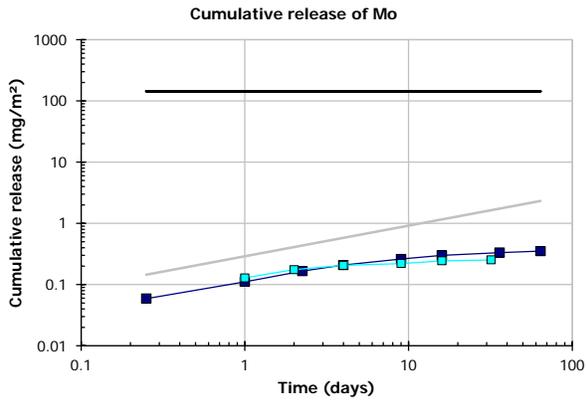
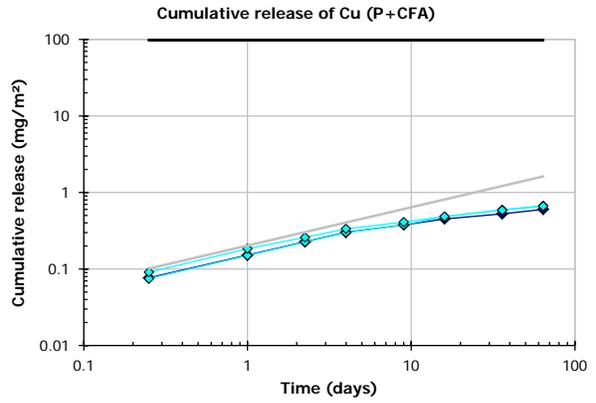
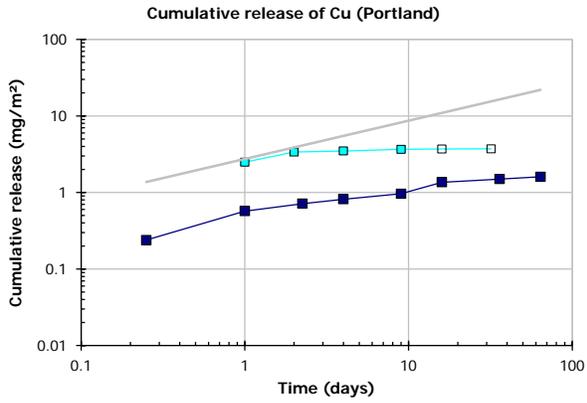
Legend:

- |                              |                                      |
|------------------------------|--------------------------------------|
| ■ Cement mortar CEM I N5     | ◆ Concrete CEM IIB V NL              |
| ■ Mortar CEM I N5 Carbonated | ◆ Concrete CEM IIB V NL Carbonated 2 |
| — NL-BBK-Open Application    | ◆ Concrete CEM IIB V NL Carbonated 1 |
| — slope=0.5                  | — NL-BBK-Open Application            |
|                              | — slope=0.5                          |

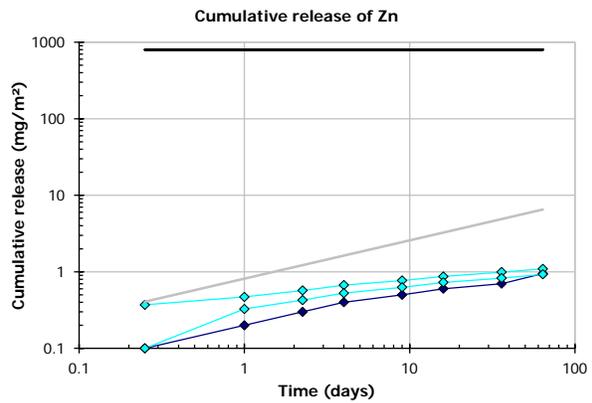
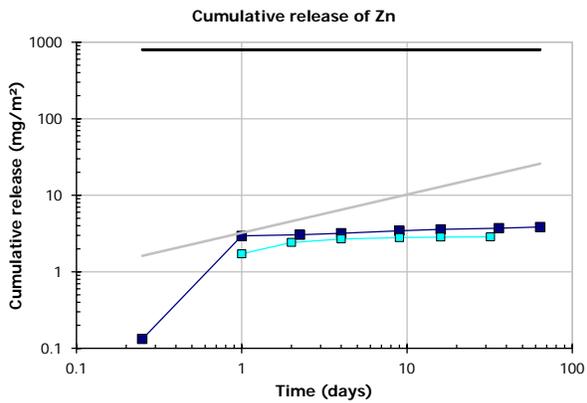
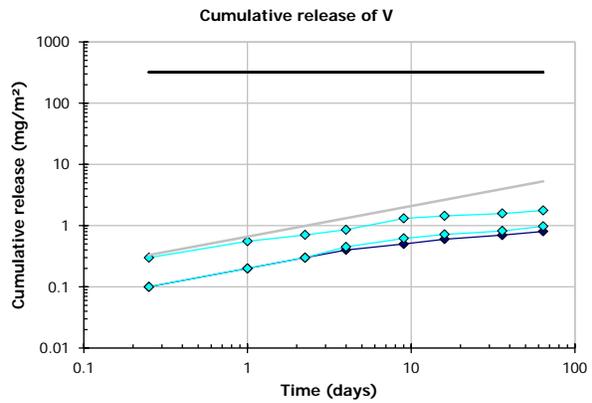
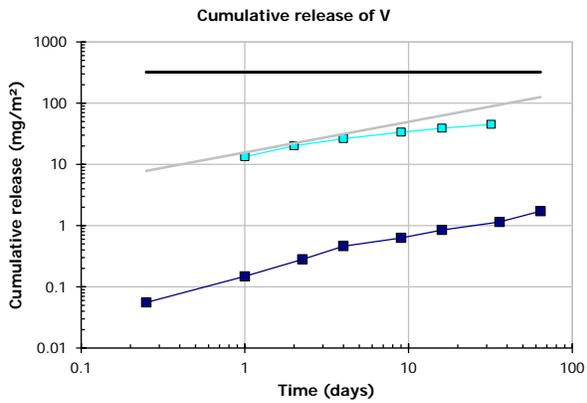
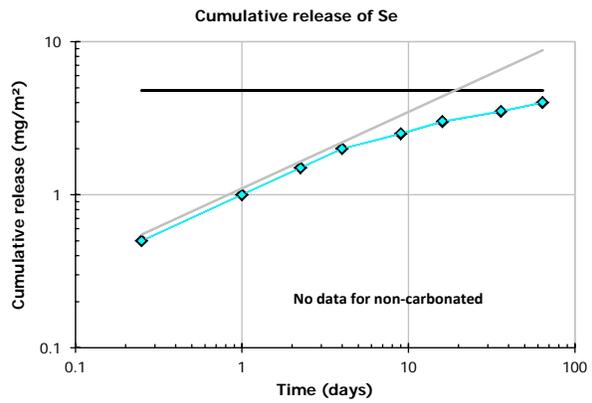
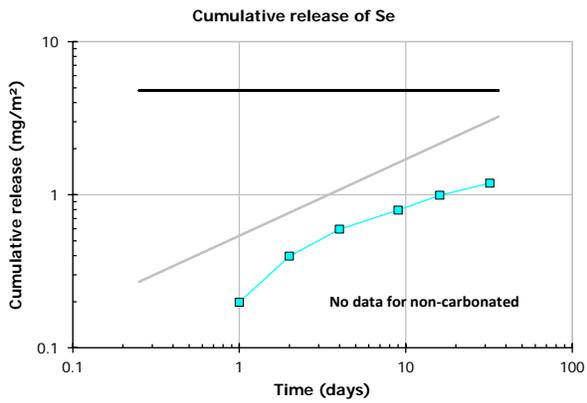
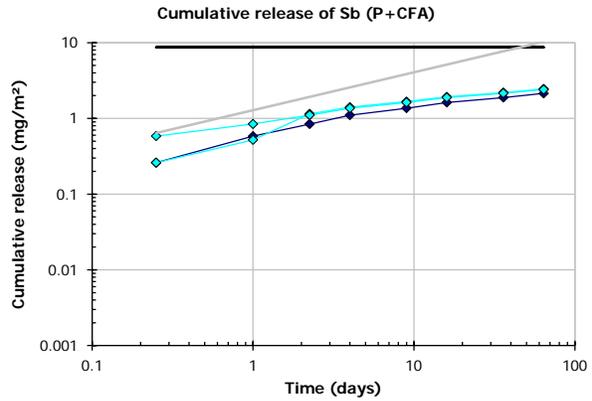
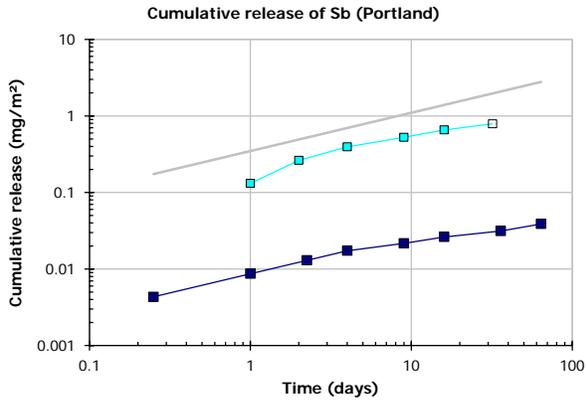
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



## **Appendix F. pH Dependent Leaching of CBP Cement Mortars and Concrete Containing Fly Ash**

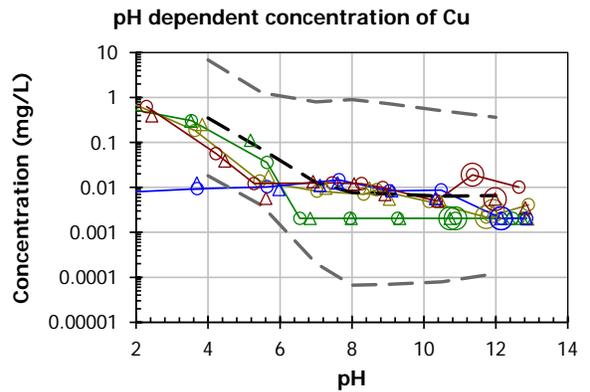
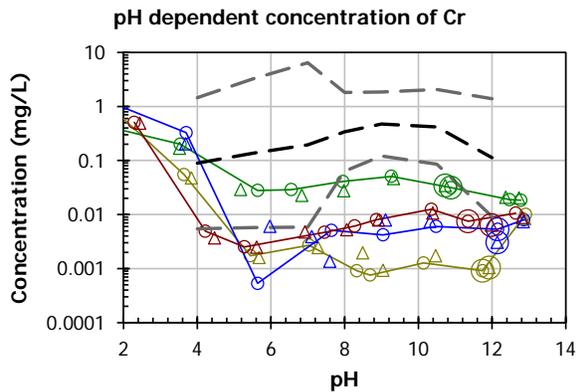
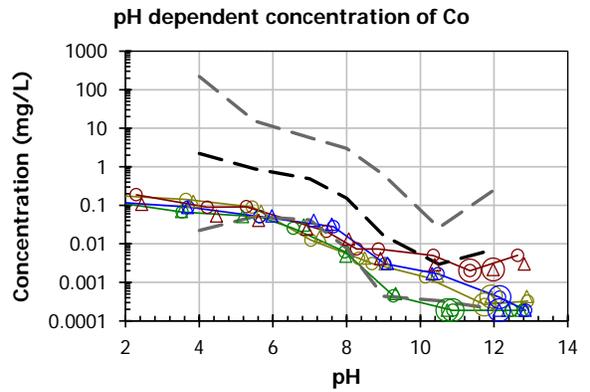
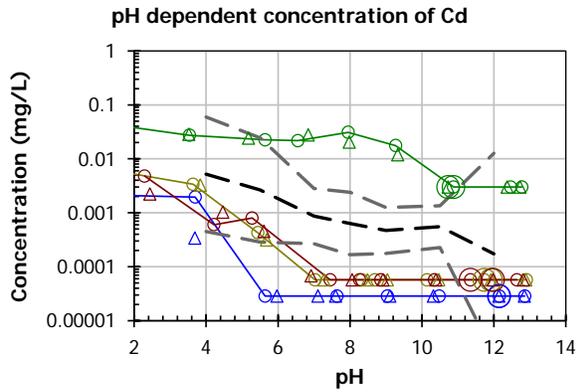
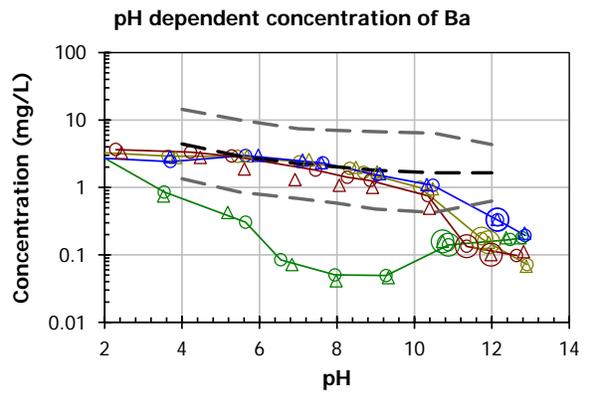
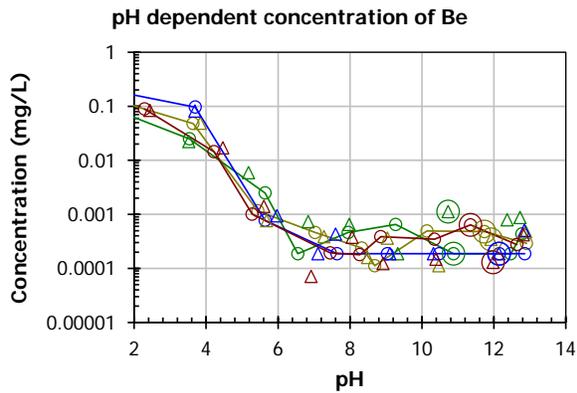
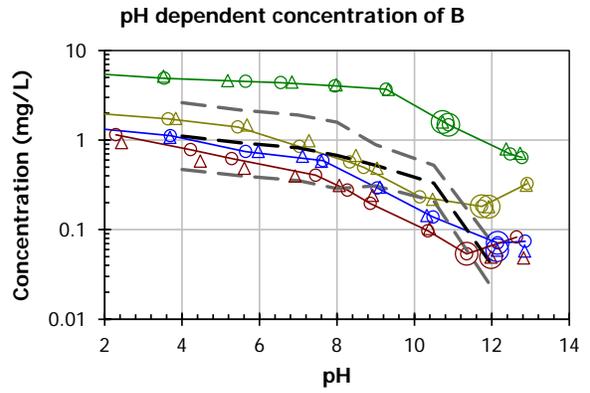
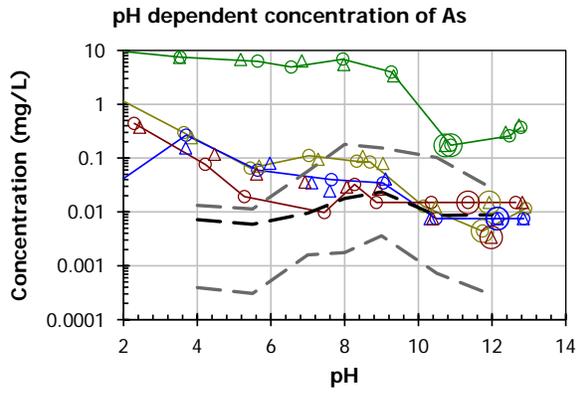
### Notes:

- Results are compared to mean and 90 percent confidence intervals of cumulative release from European cement mortars and concrete containing fly ash (CEM II/B-V) as presented in Appendix A.

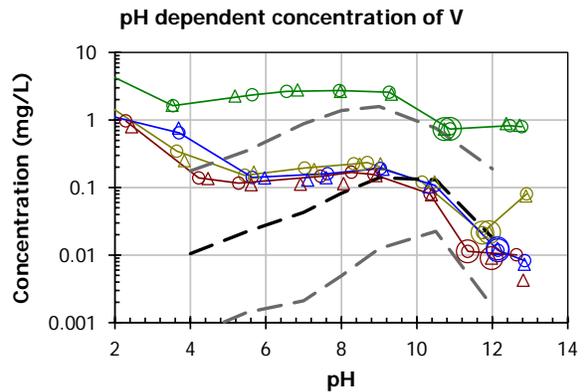
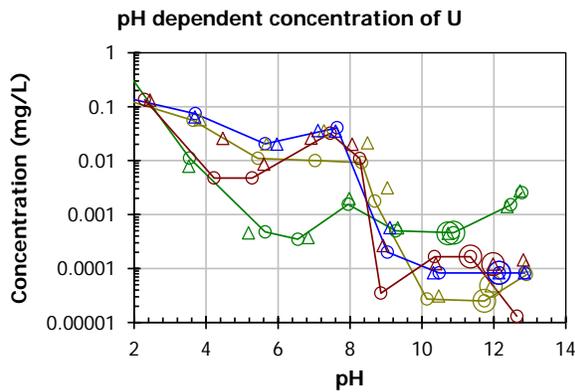
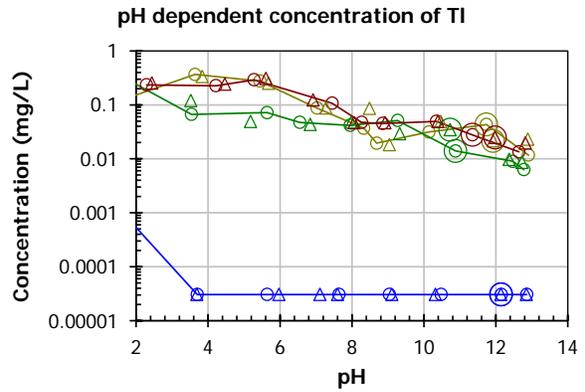
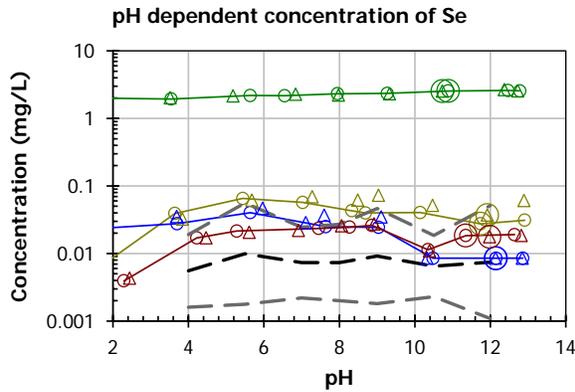
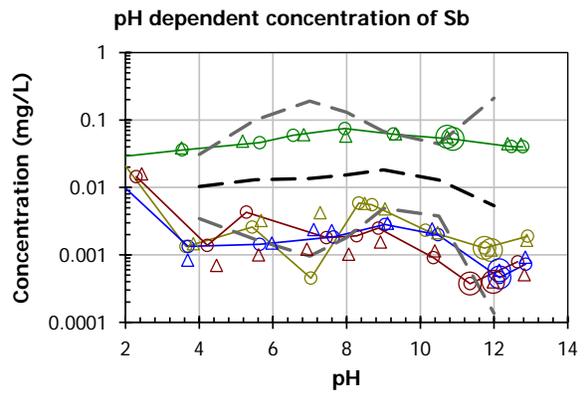
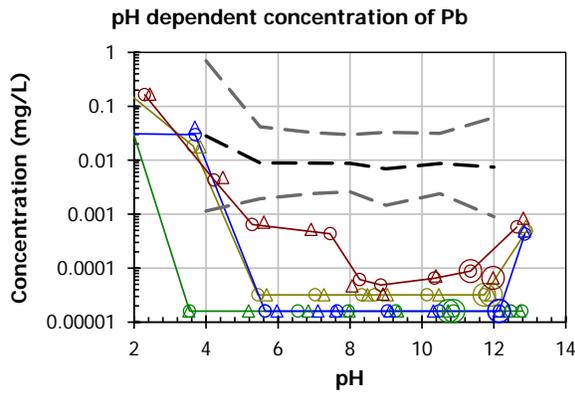
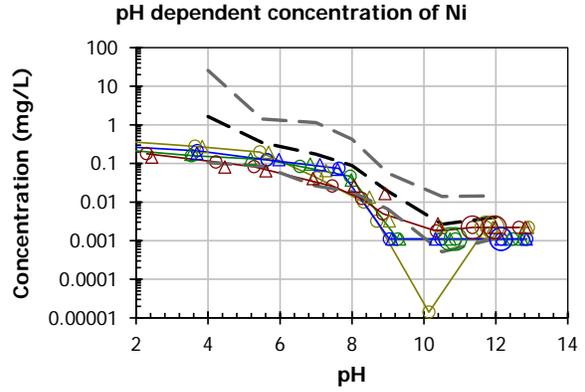
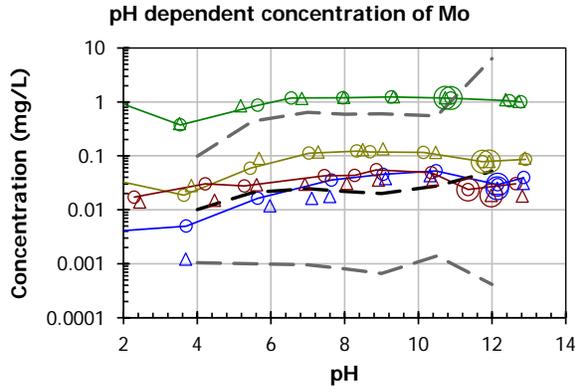
### Legend:

—○— BGM(P,1,1)	○ own pH	—△— BGM(P,1,2)	○ own pH
—○— FAF(P,1,1)	○ own pH	—△— FAF(P,1,2)	○ own pH
—○— SVC(P,1,1)	○ own pH	—△— SVC(P,1,2)	○ own pH
—○— VCT(P,1,1)	○ own pH	—△— VCT(P,1,2)	○ own pH

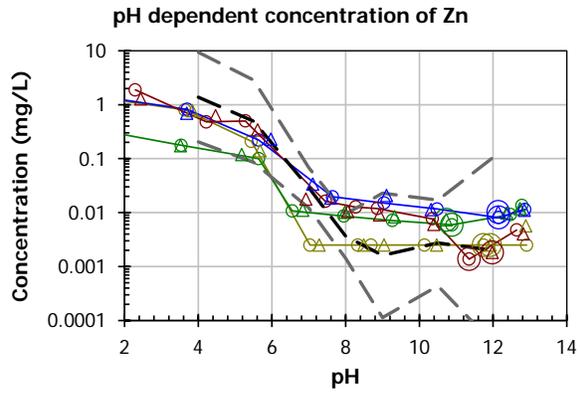
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

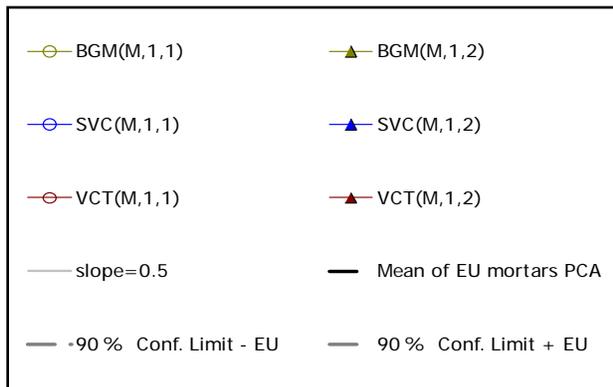


## **Appendix G. Cumulative Release from Monolith Leaching of CBP Cement Mortars and Concrete Containing Fly Ash**

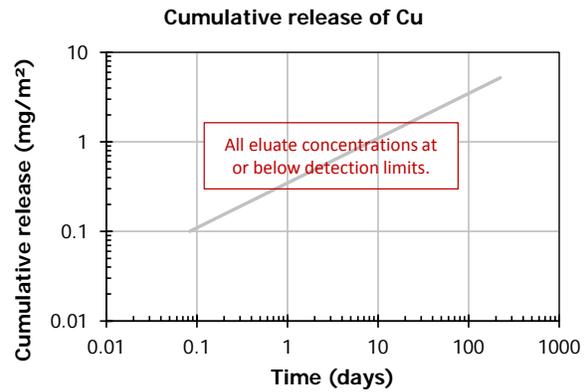
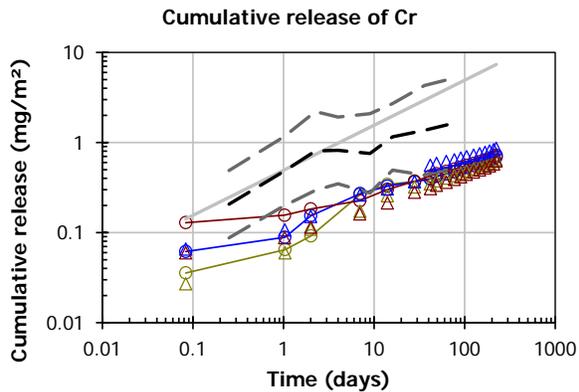
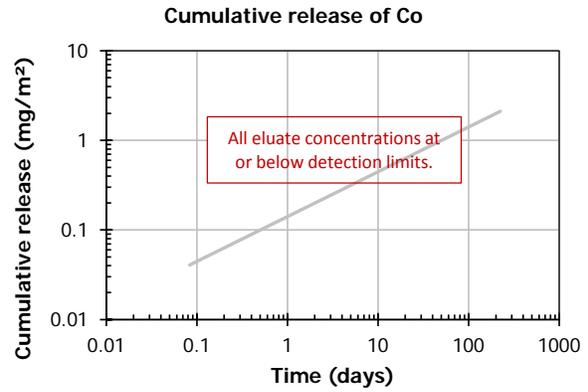
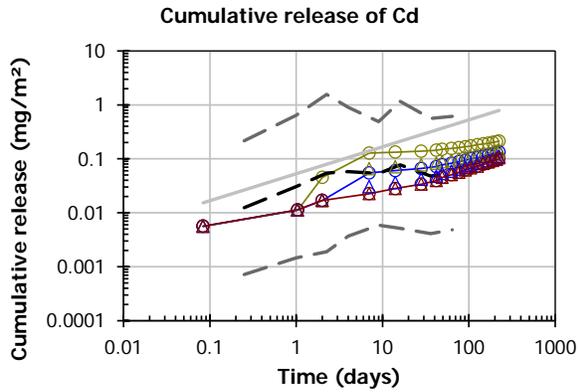
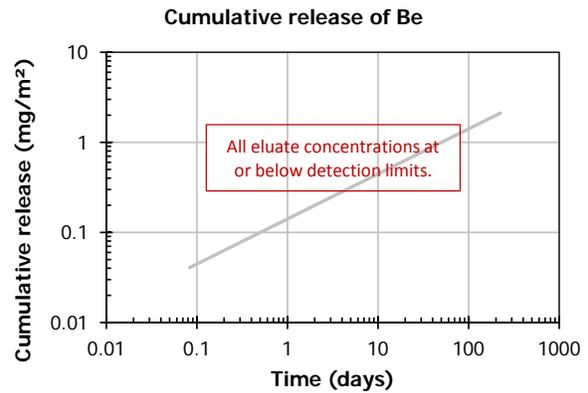
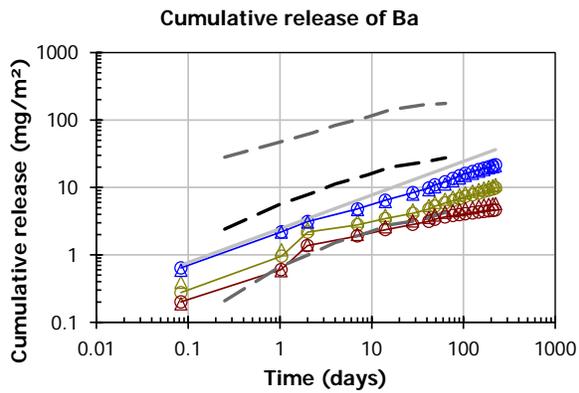
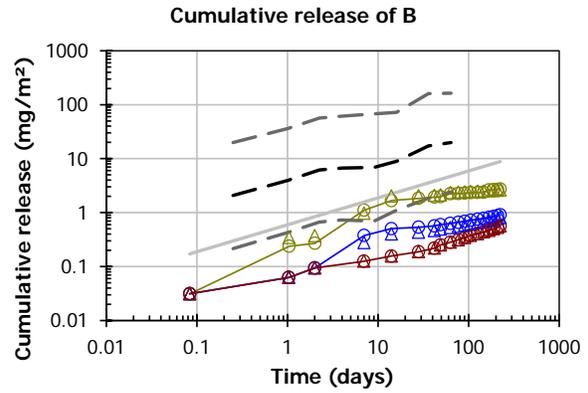
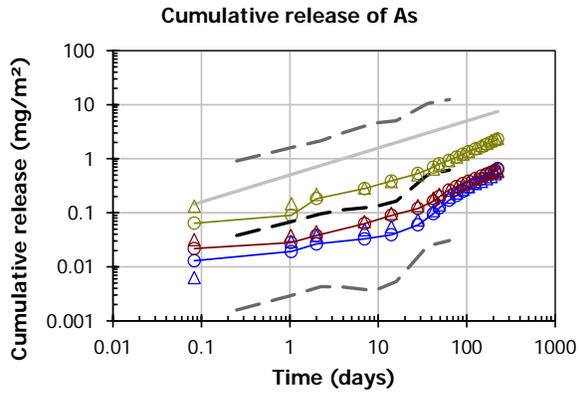
**Notes:**

- Results are compared to the mean and 90 percent confidence intervals of cumulative release from EU cement mortars and concrete containing fly ash (CEM II/B-V) as presented in Appendix C.

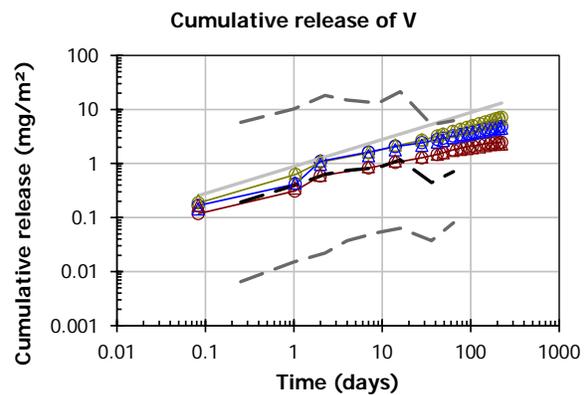
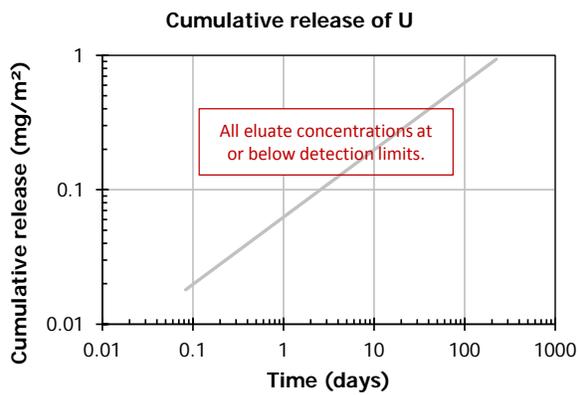
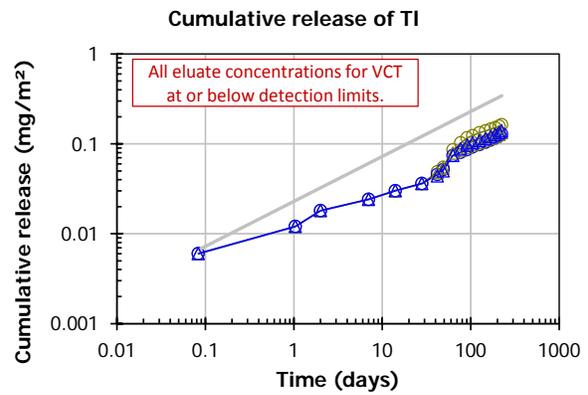
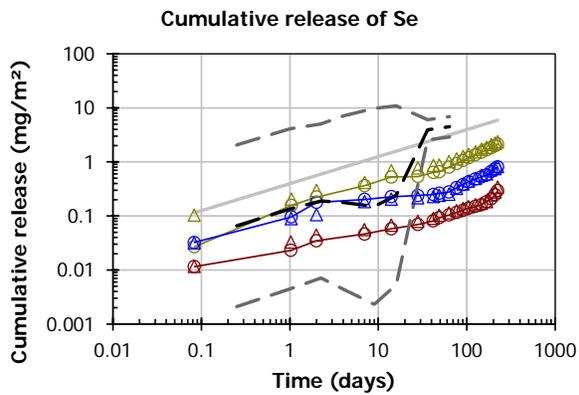
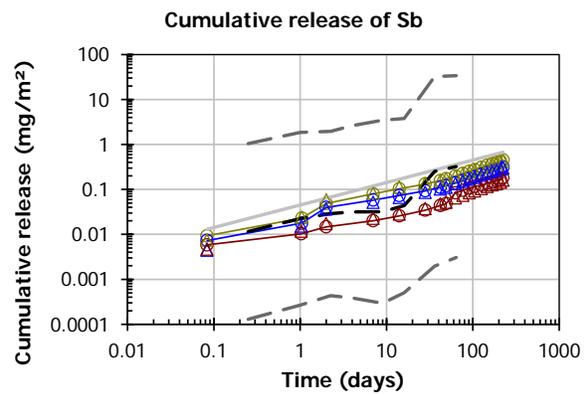
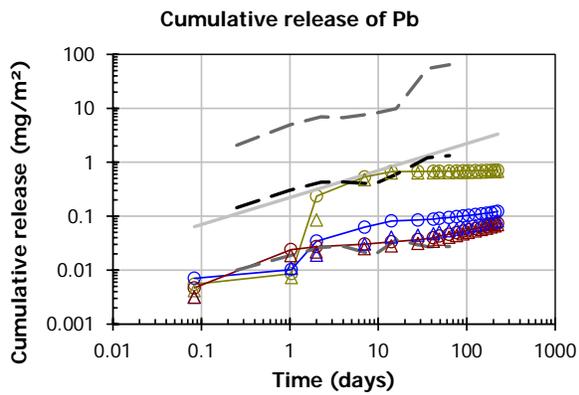
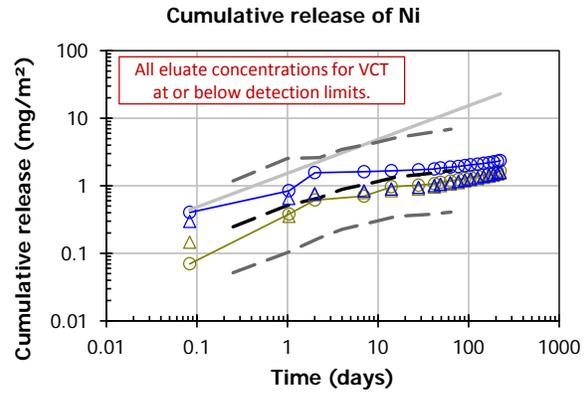
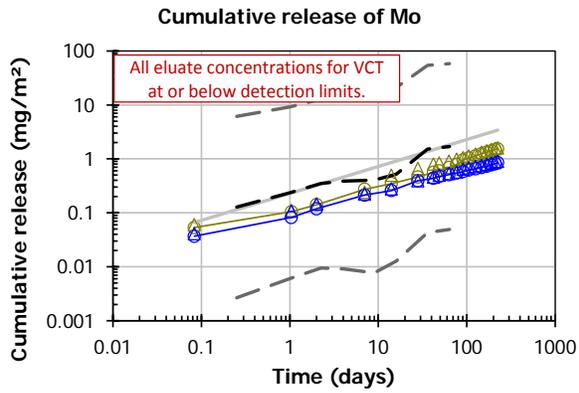
**Legend:**



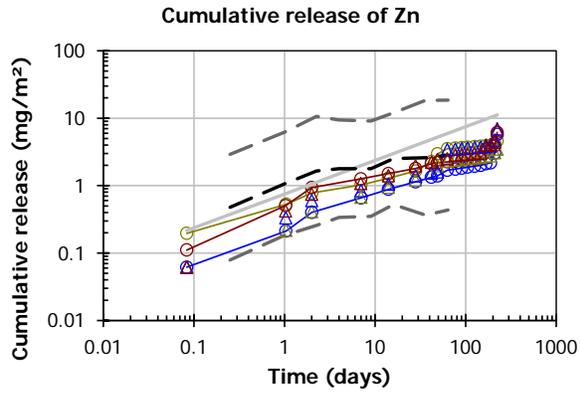
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

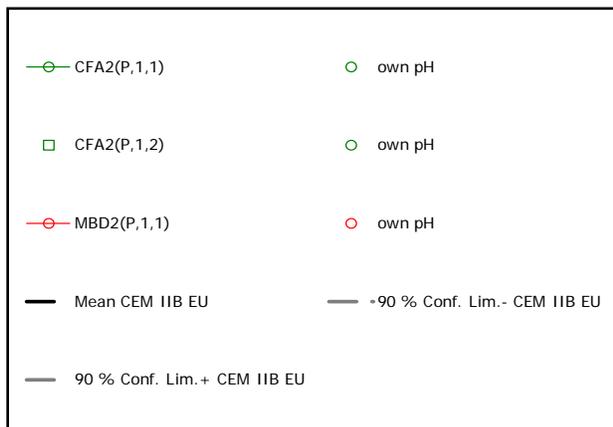


## **Appendix H. pH Dependent Leaching of a Fly Ash (CFA2) and a Fly Ash-Containing Cement Mortar (MBD2)**

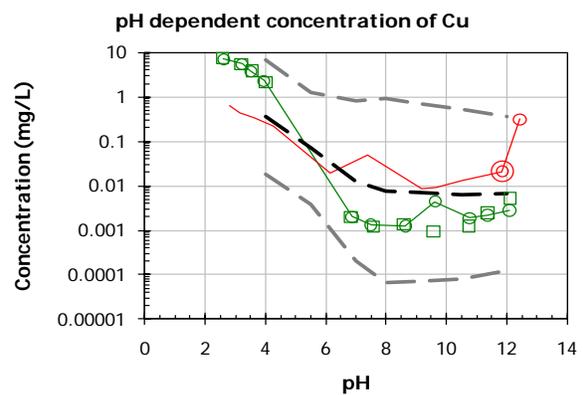
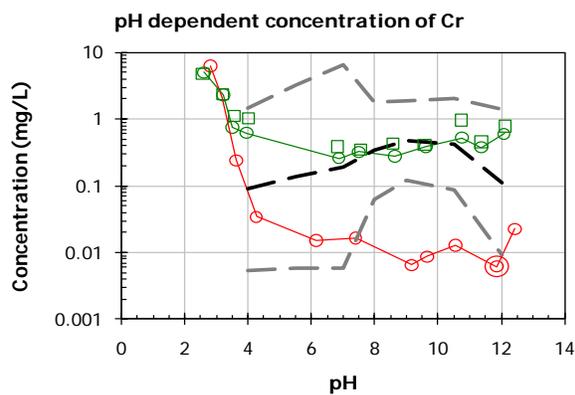
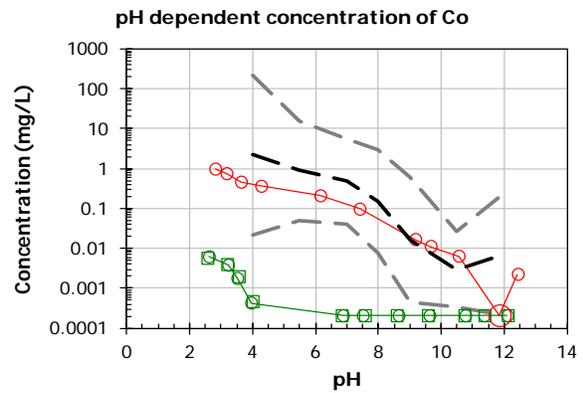
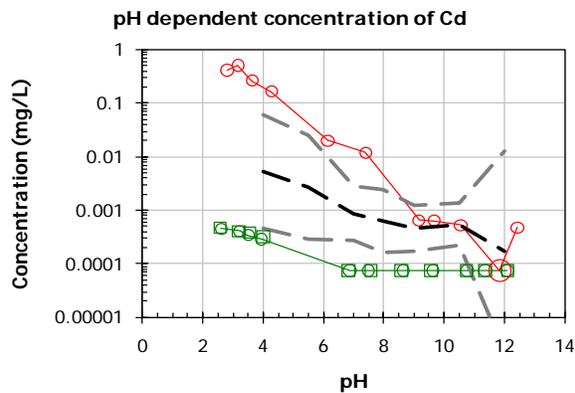
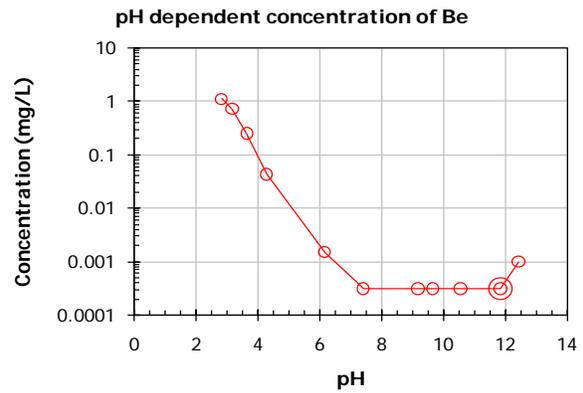
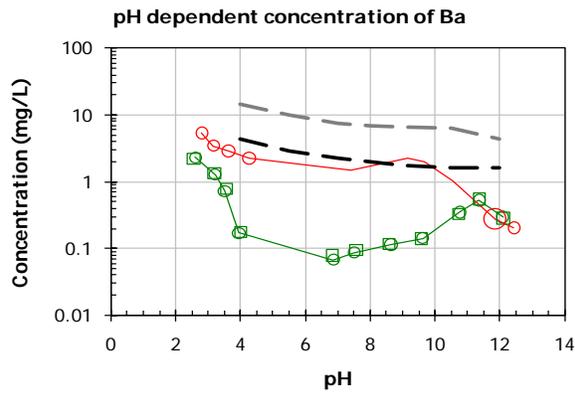
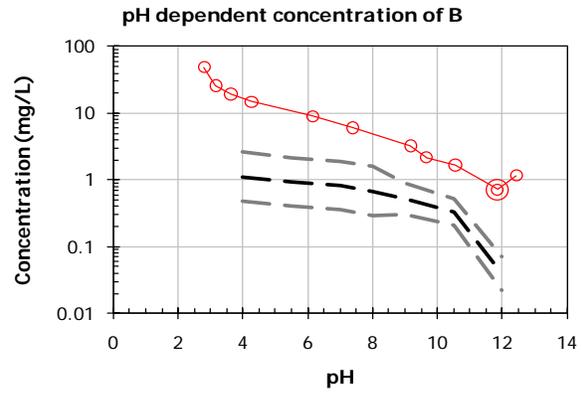
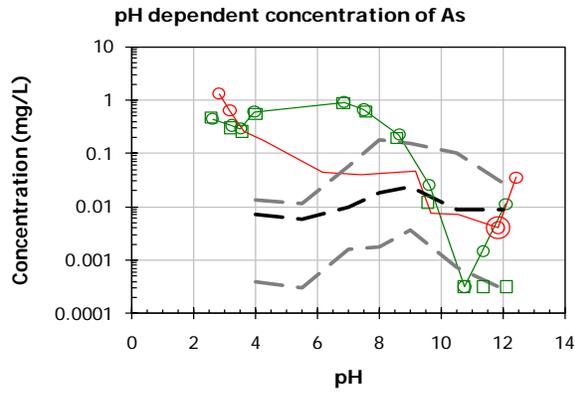
### Notes:

- Results are compared to mean and 90 percent confidence intervals of cumulative release from EU cement mortars and concrete containing fly ash (CEM II/B-V) as presented in Appendix A.

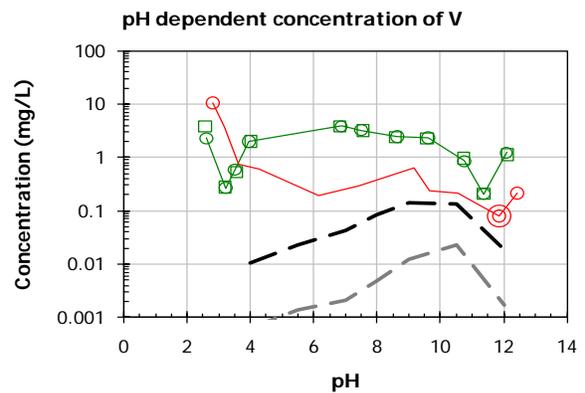
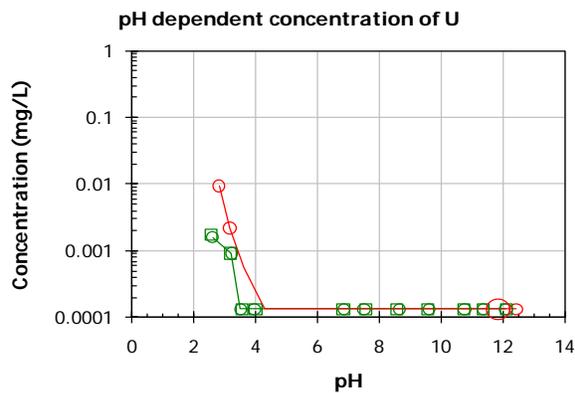
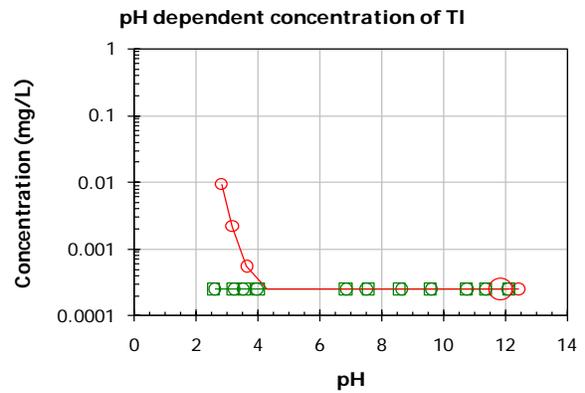
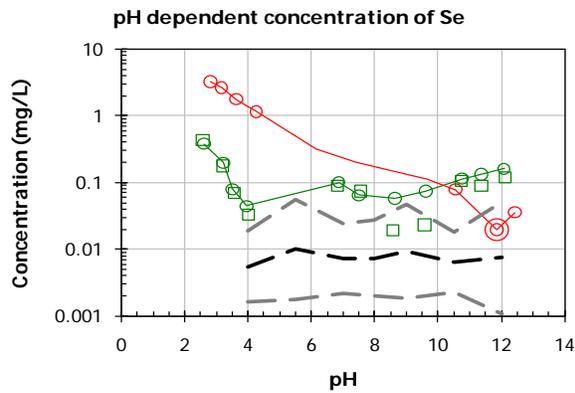
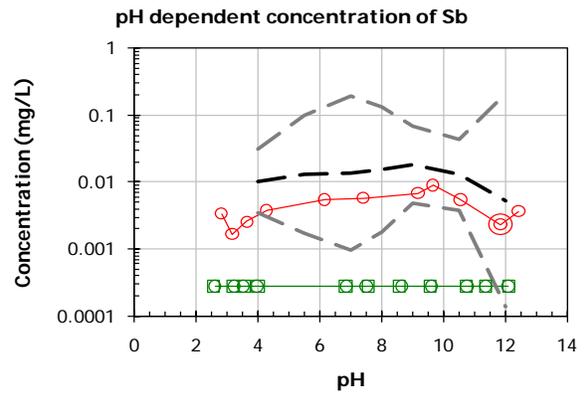
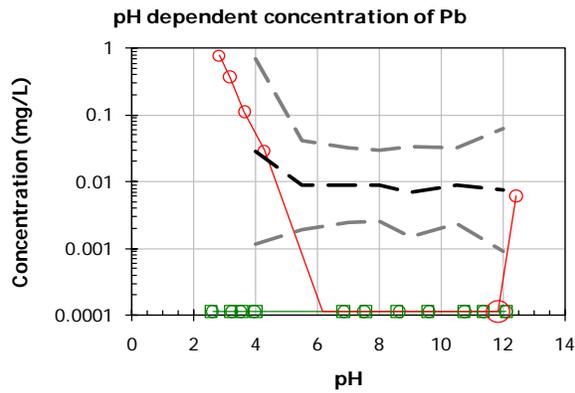
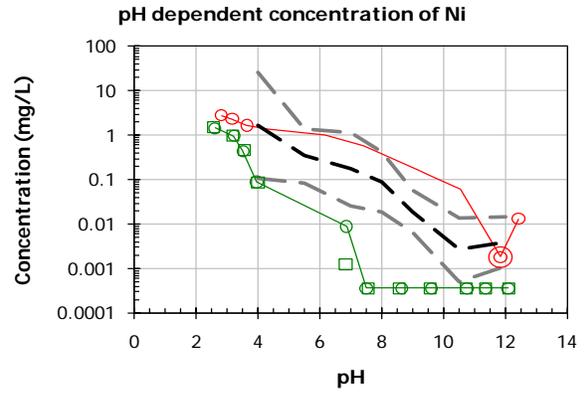
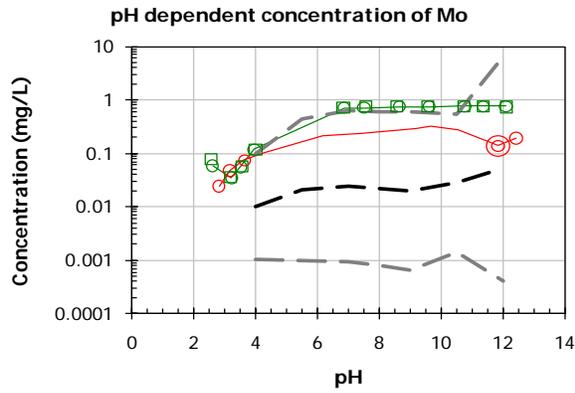
### Legend:



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

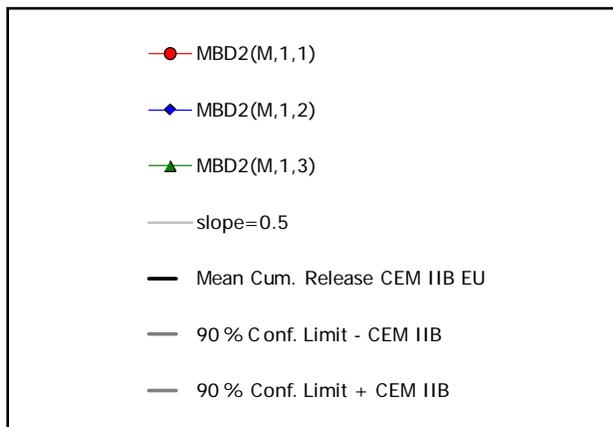


## **Appendix I. Cumulative Release from Monolith Leaching of a Fly Ash-Containing Cement Mortar (MBD2)**

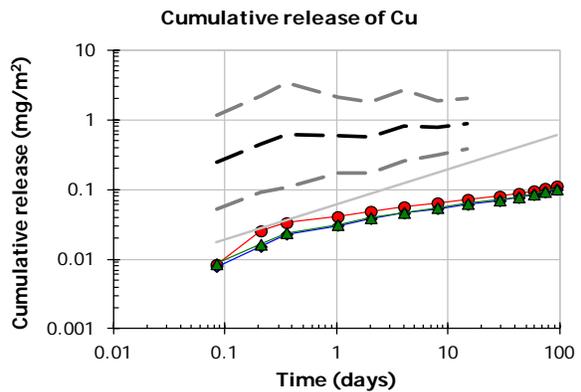
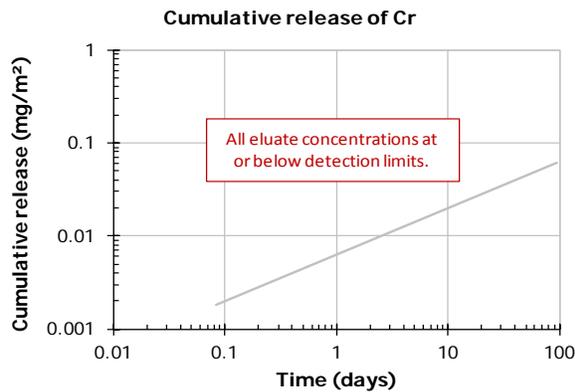
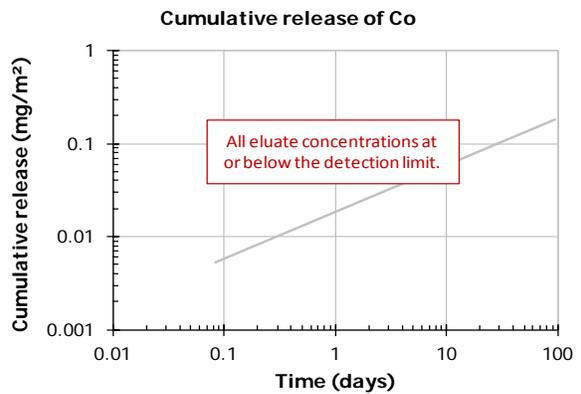
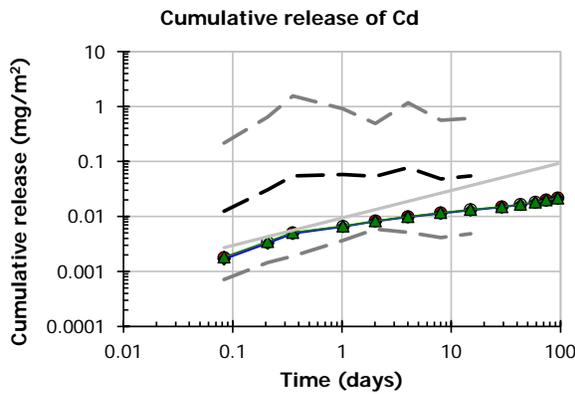
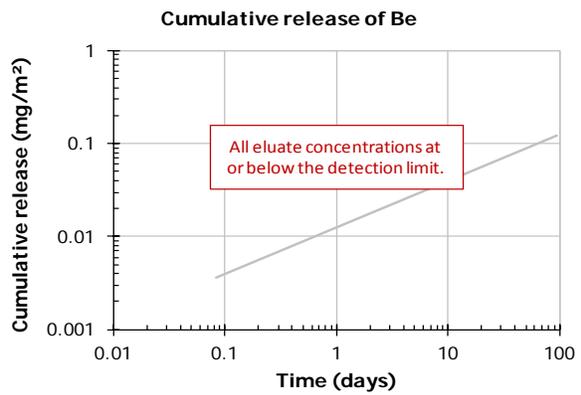
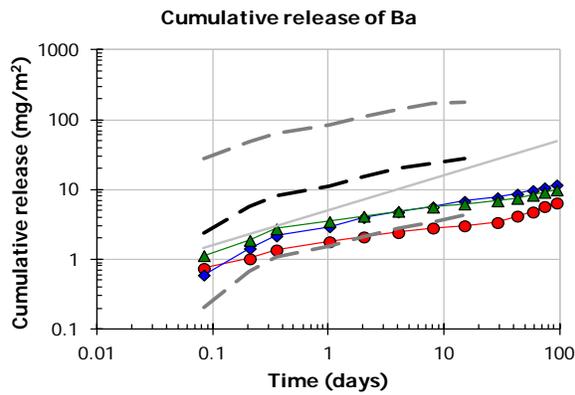
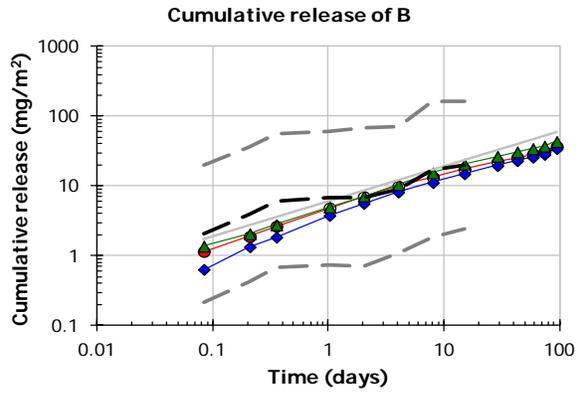
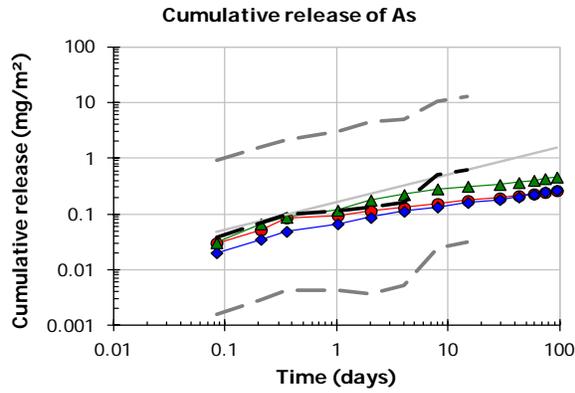
### Notes:

- Results are compared to mean and 90 percent confidence intervals of cumulative release from EU cement mortars and concrete containing fly ash (CEM II/B-V) as presented in Appendix C. A gray solid diagonal line is included as a reference line indicating ideal simple Fickian diffusion controlled release behavior.

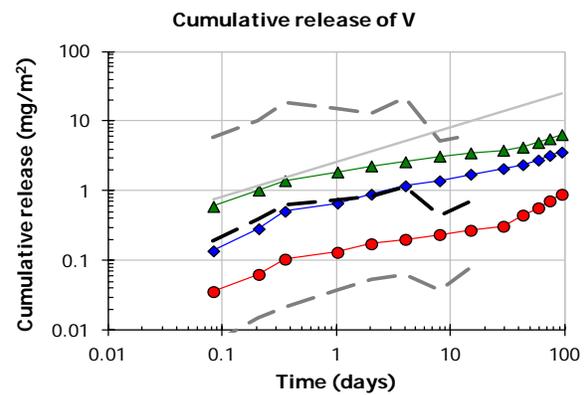
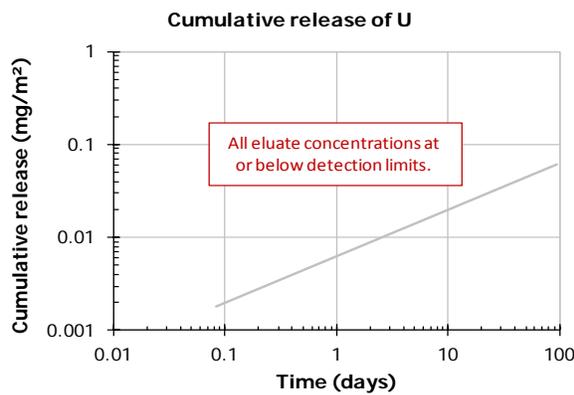
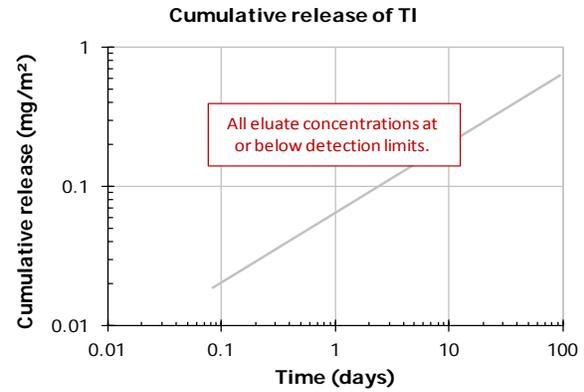
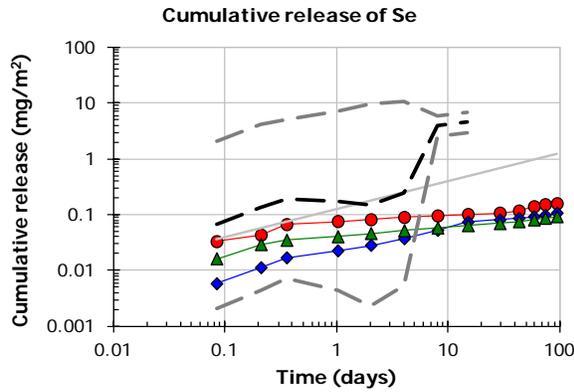
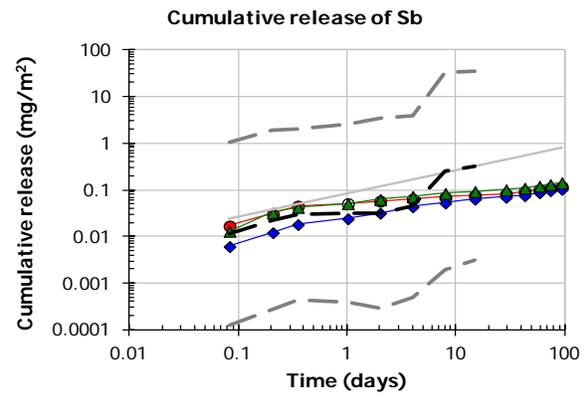
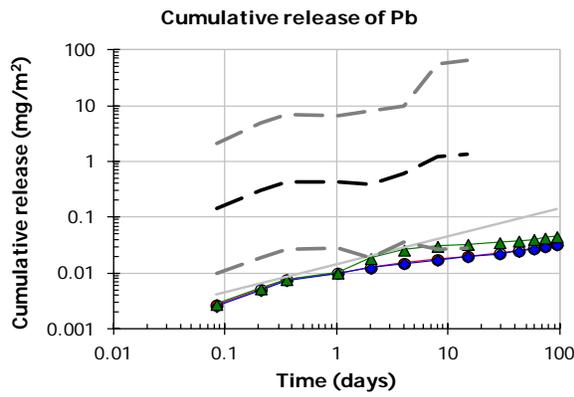
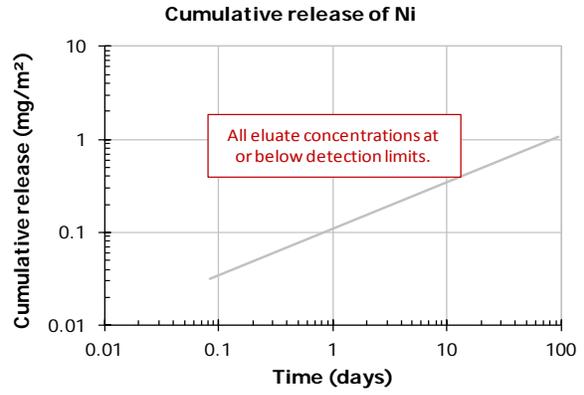
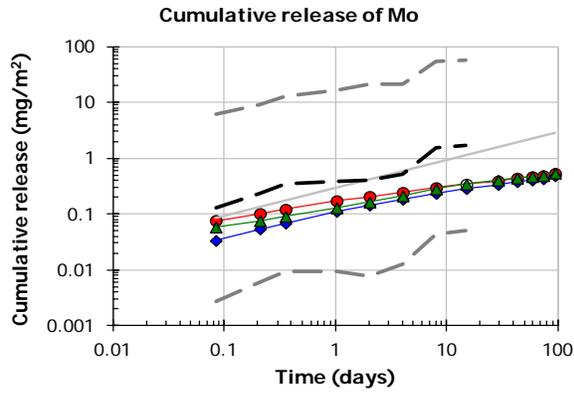
### Legend:



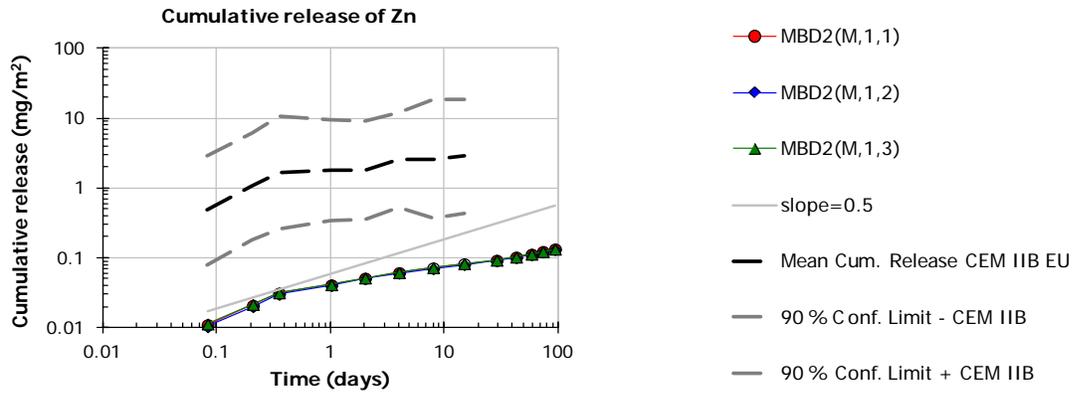
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes

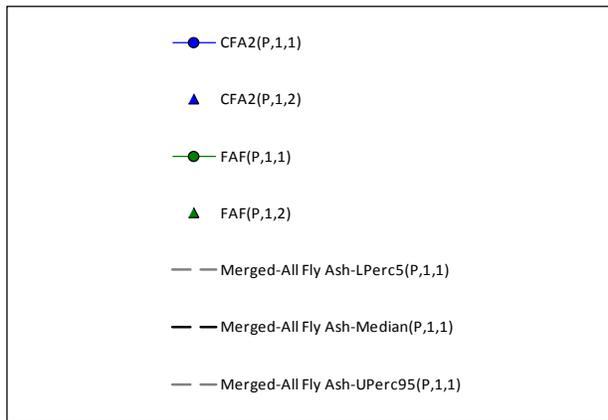


## **Appendix J. pH Dependent Leaching of Fly Ash Samples (FAF and CFA2) Compared to the Range of USEPA Fly Ash Leaching Data**

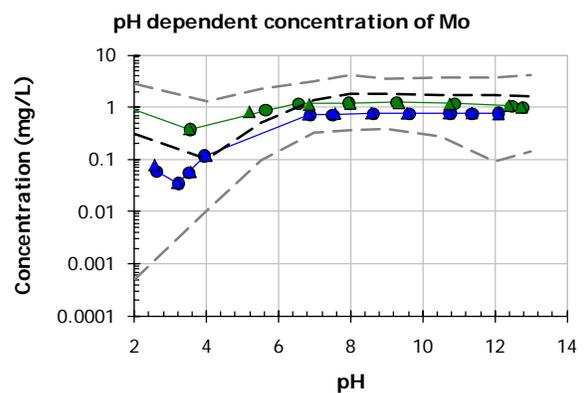
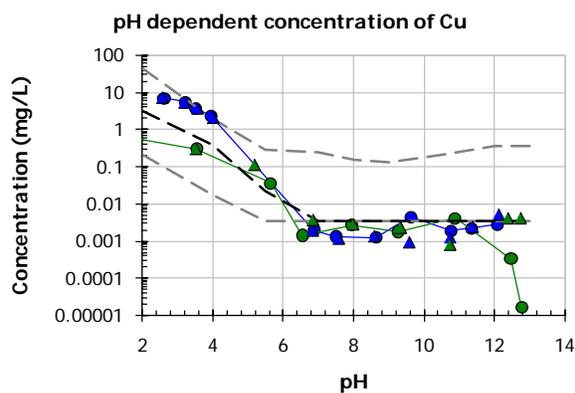
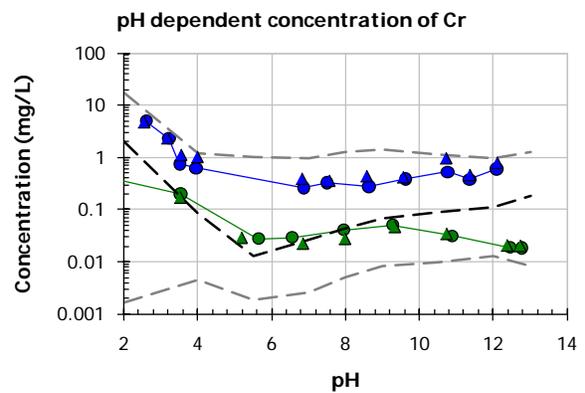
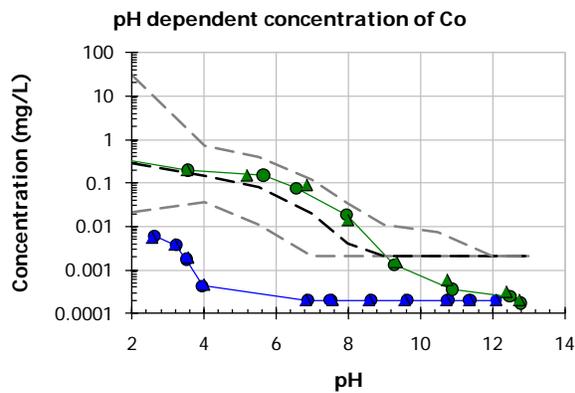
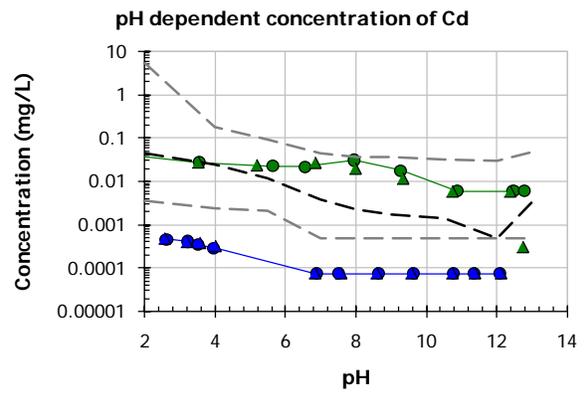
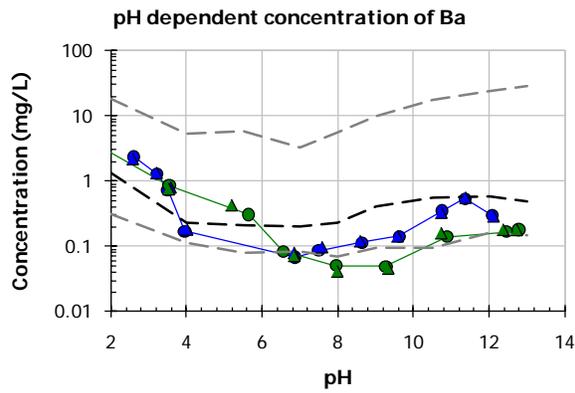
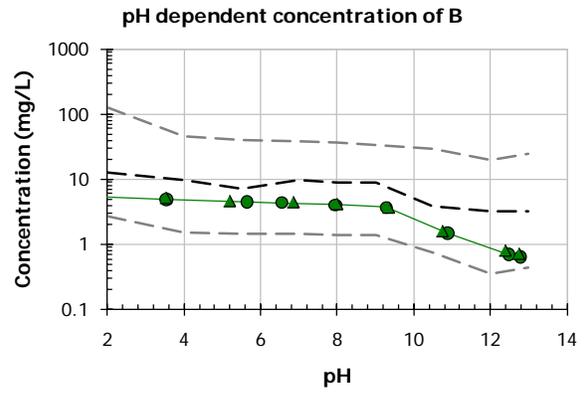
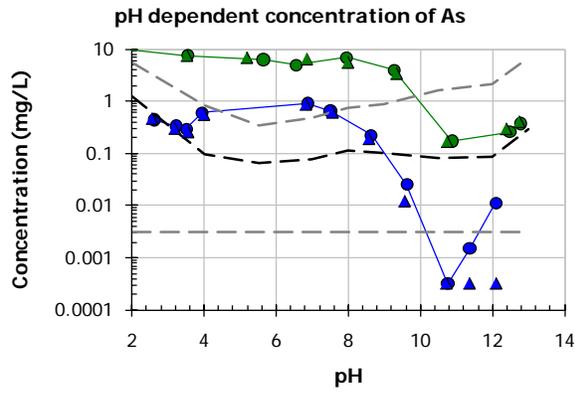
### Notes:

- Results for FAF and CFA2 are compared to the mean, 5<sup>th</sup> and 95<sup>th</sup> percentiles for all fly ash samples in Kosson et al. (2009) plus EaFA from Garrabrants et al. (2012).

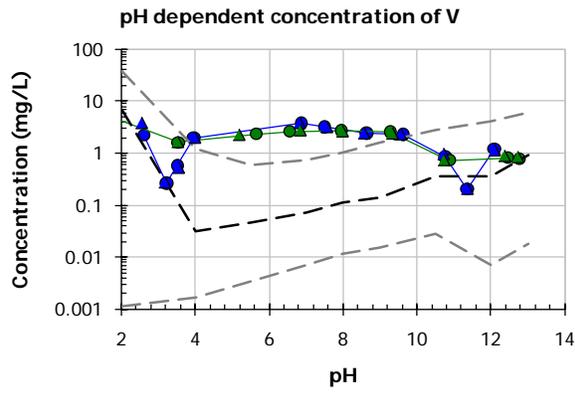
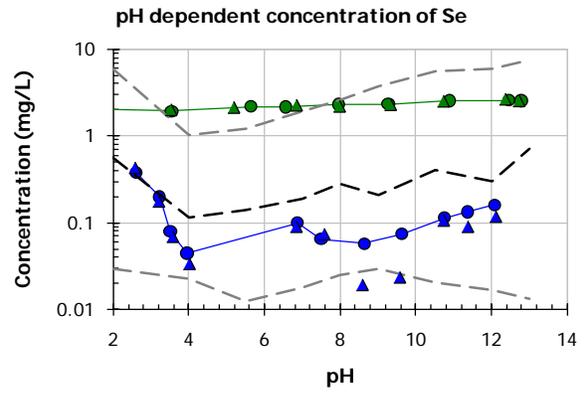
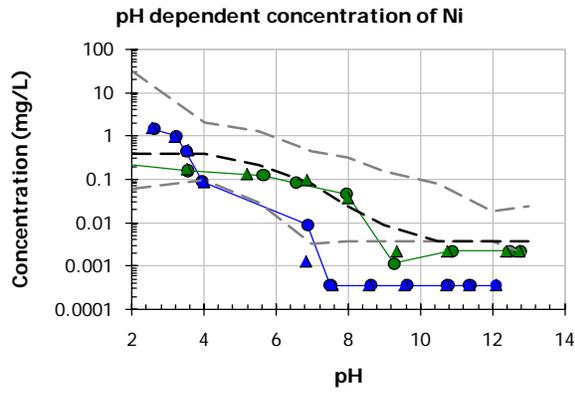
### Legend:



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

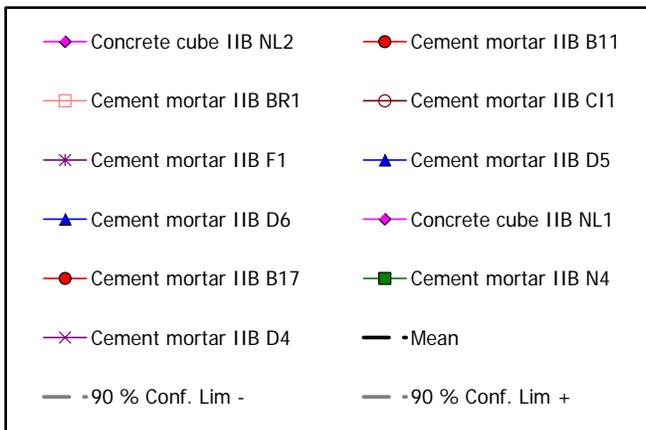
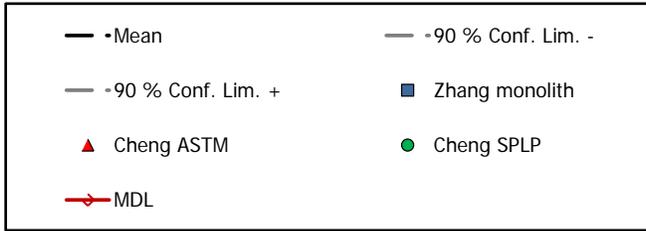


*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

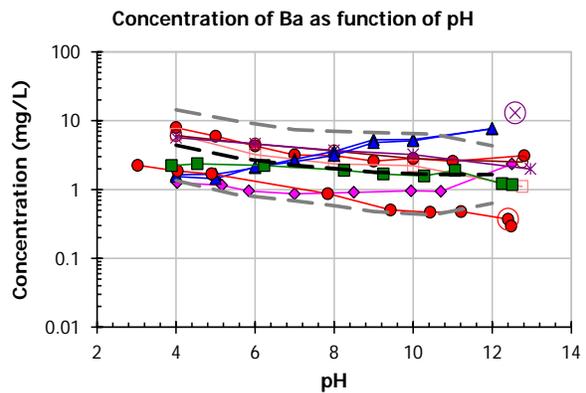
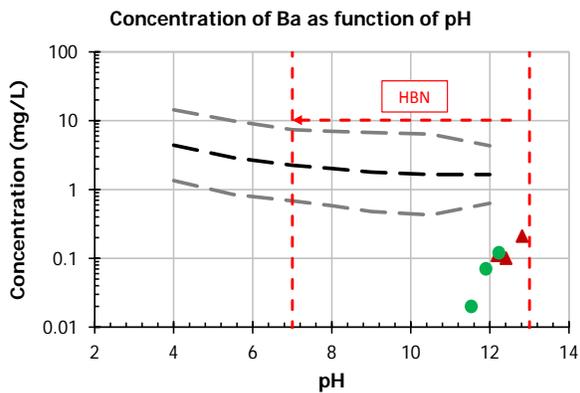
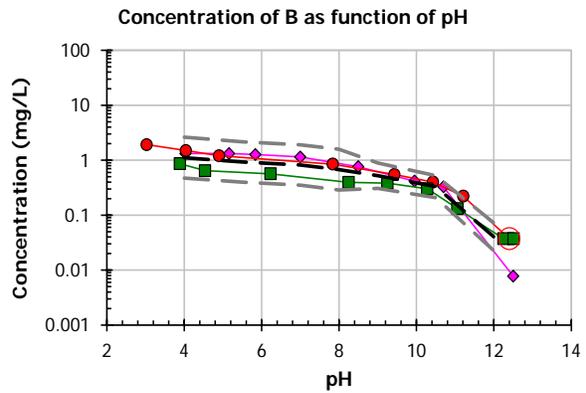
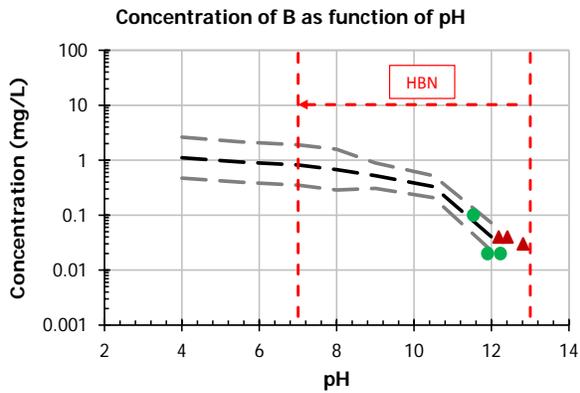
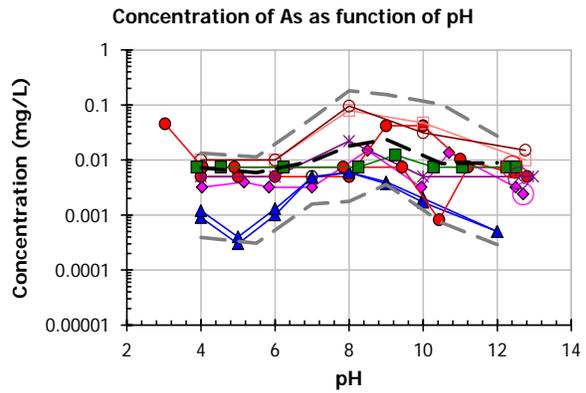
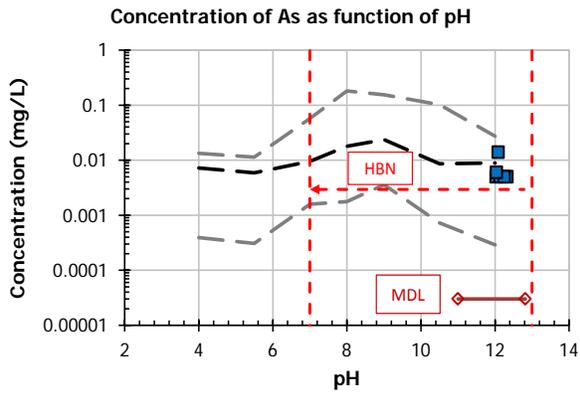
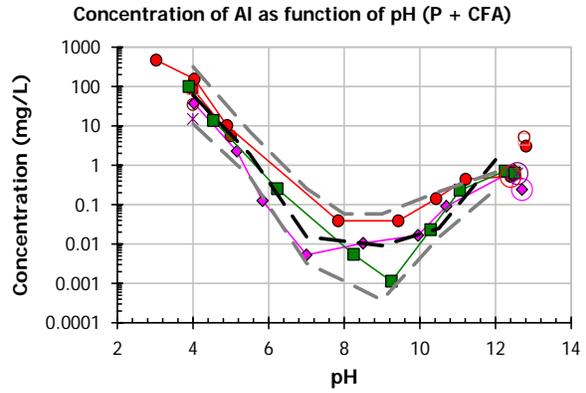
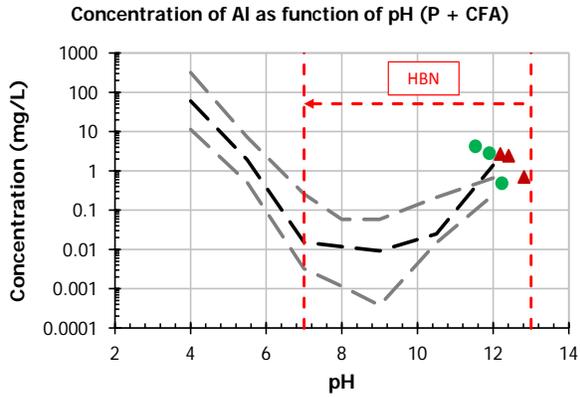


**Appendix K. pH Dependent Leaching of EU CEM II/V-B and Single Extraction Leaching Results (Cheng et al., 2008 and Zhang et al., 2001) Compared to the USEPA Health-based Numbers**

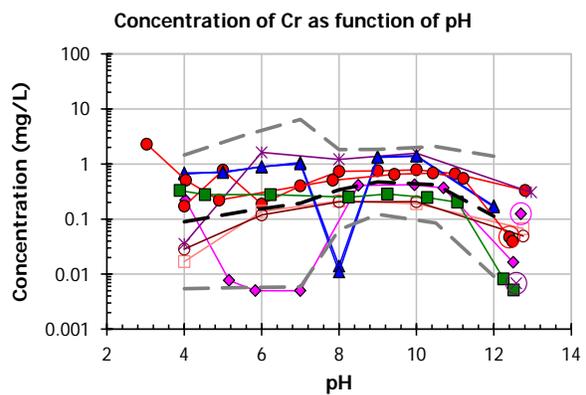
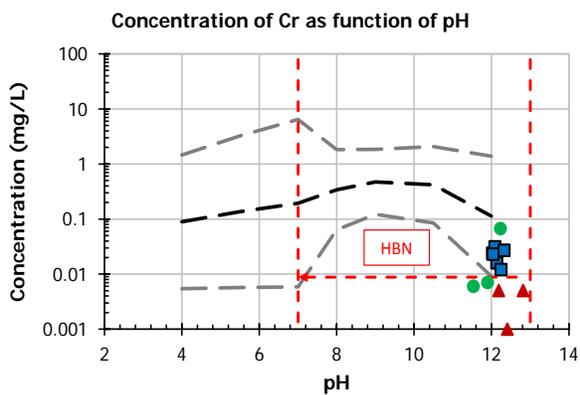
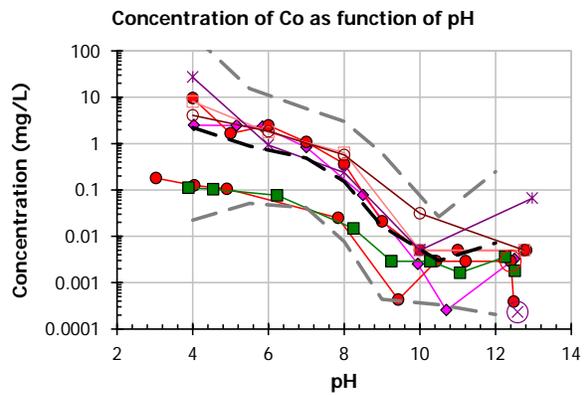
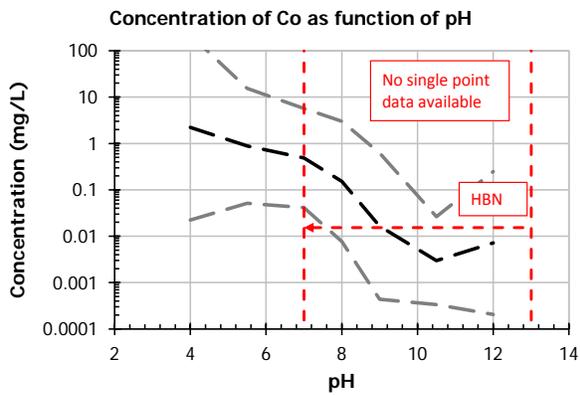
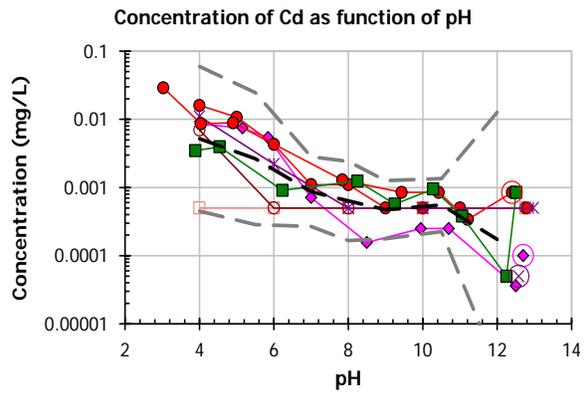
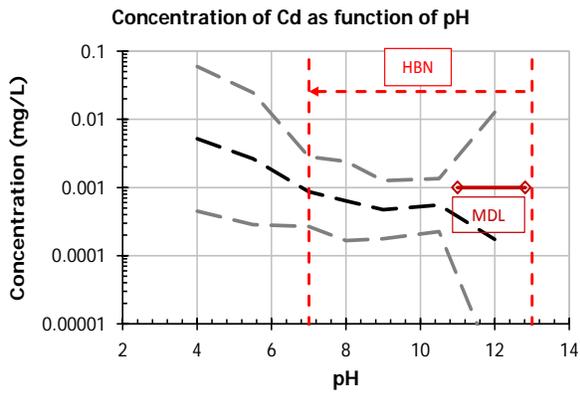
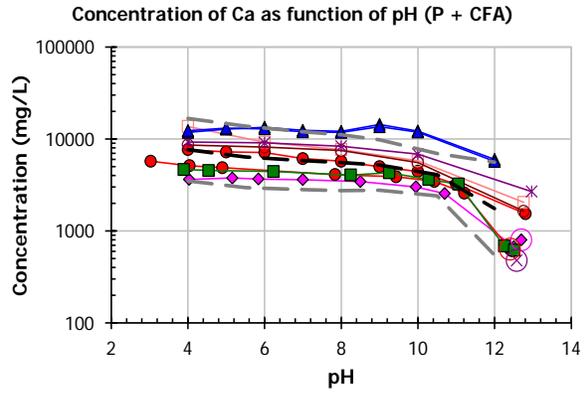
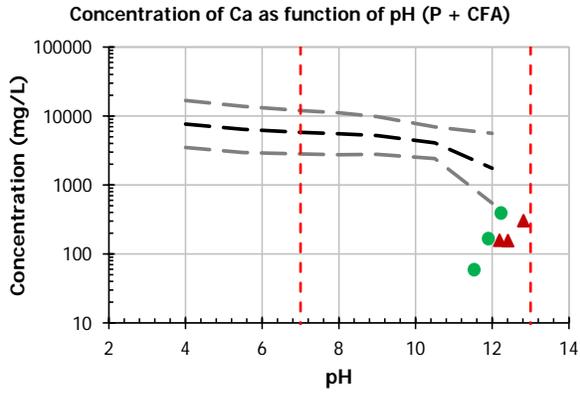
Legend:



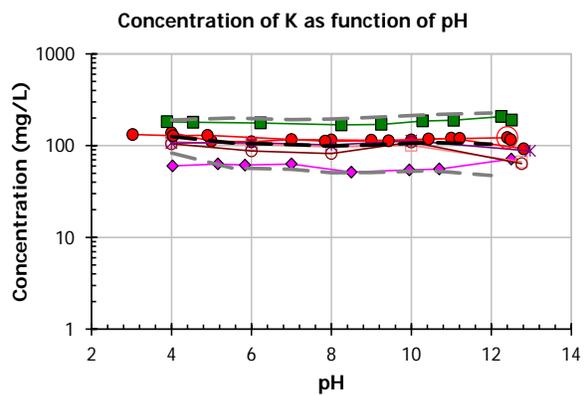
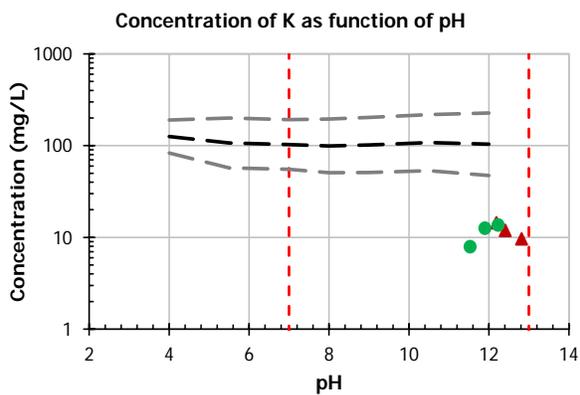
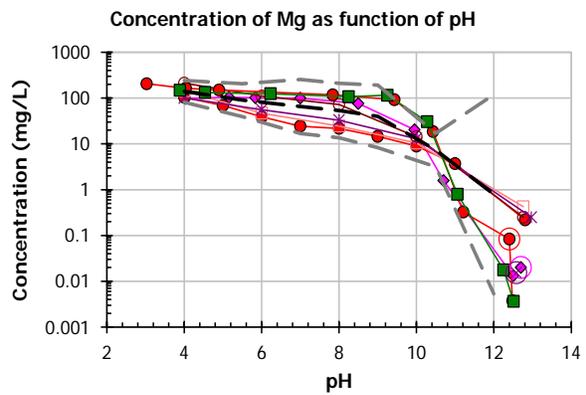
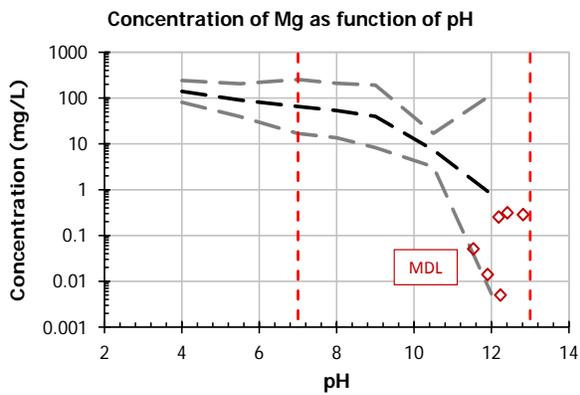
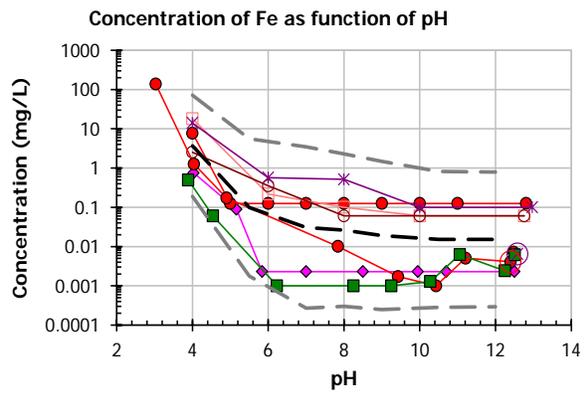
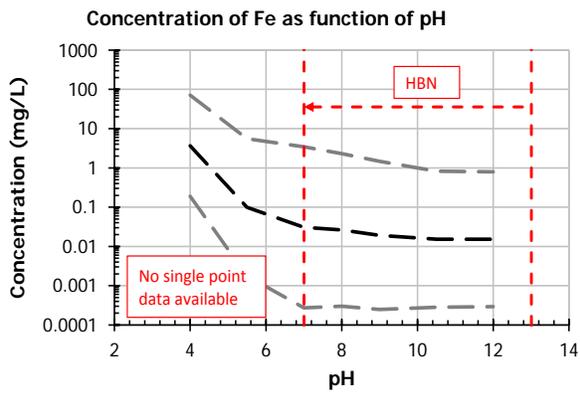
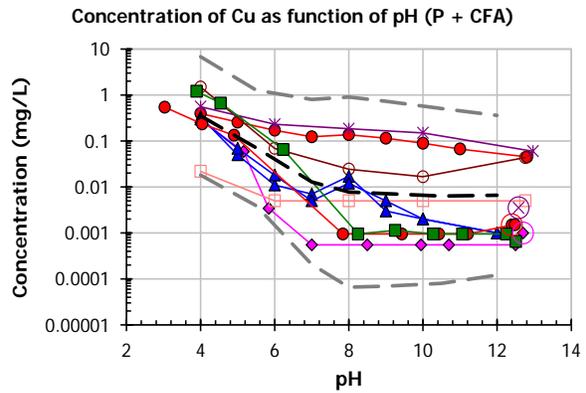
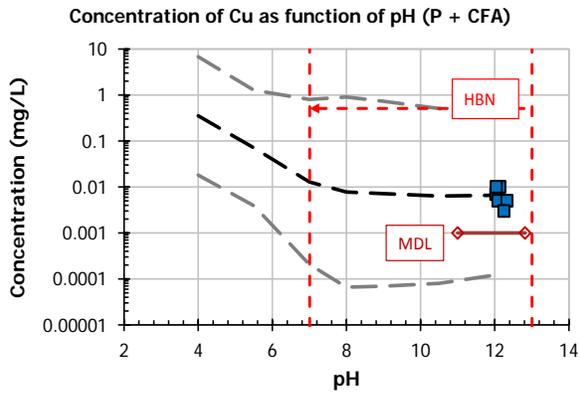
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



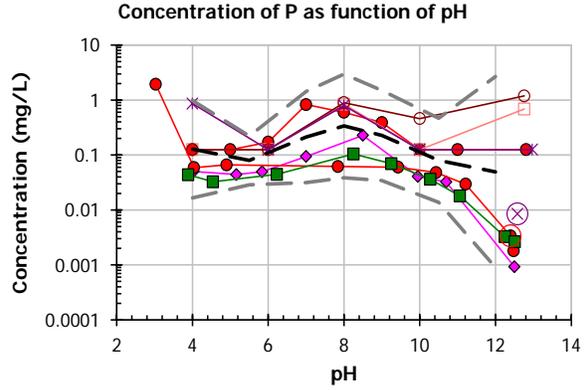
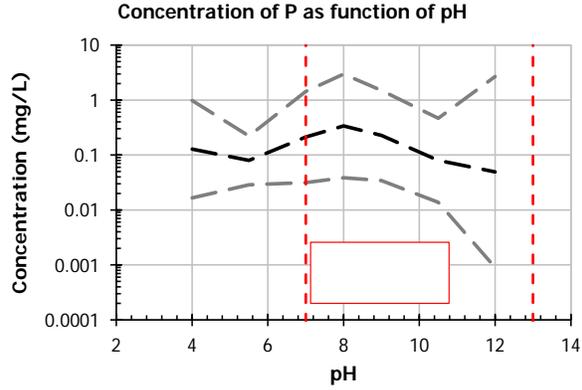
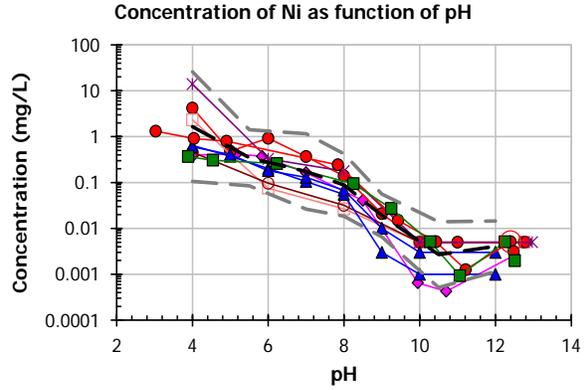
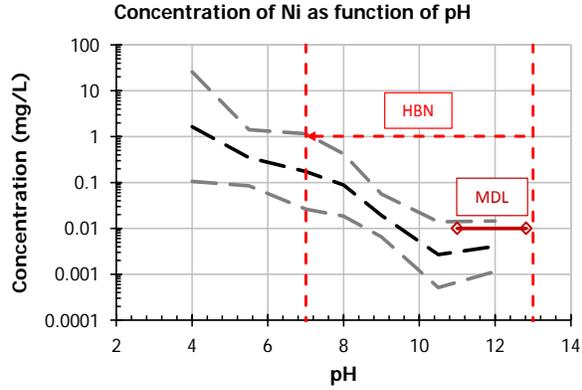
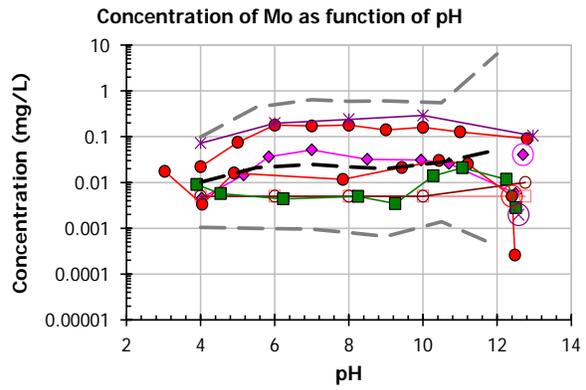
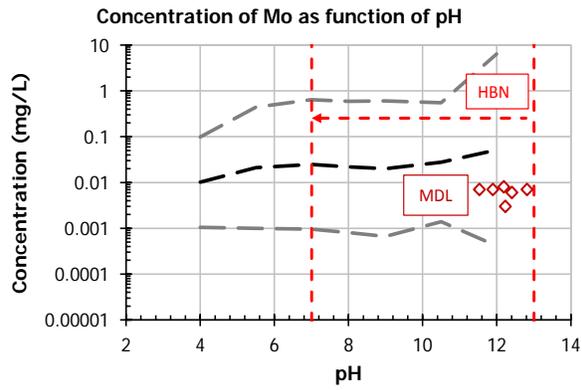
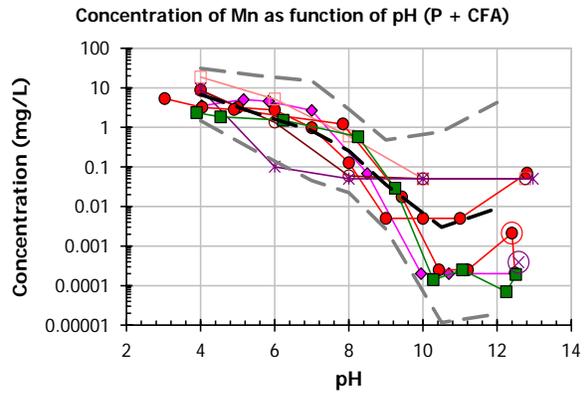
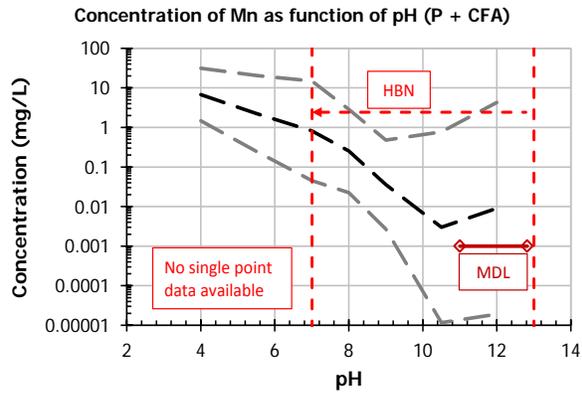
The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes



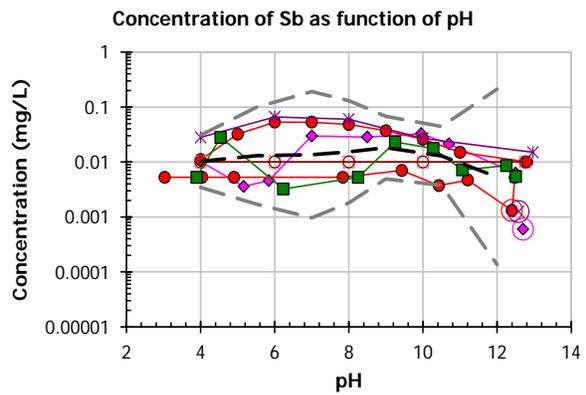
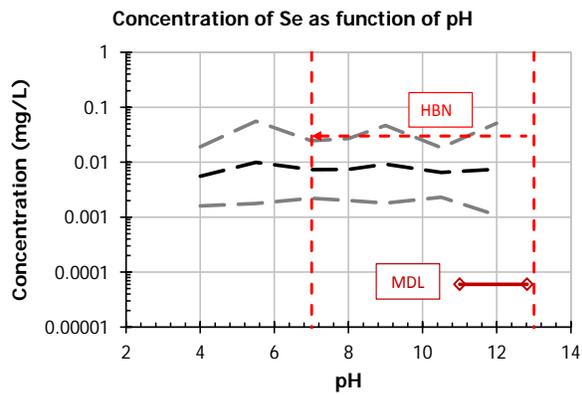
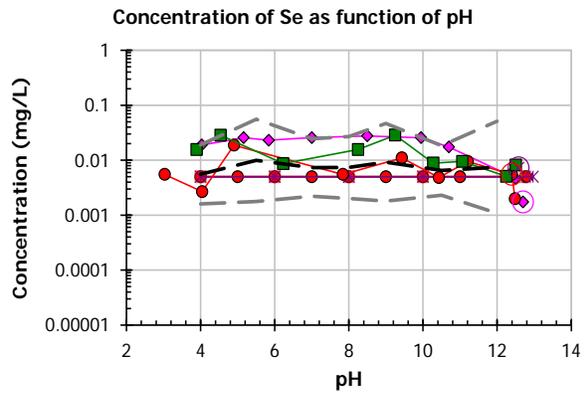
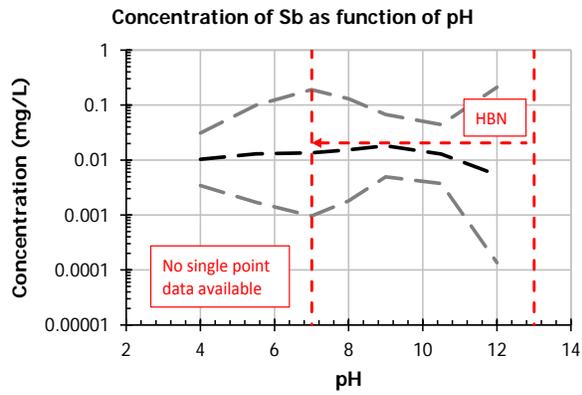
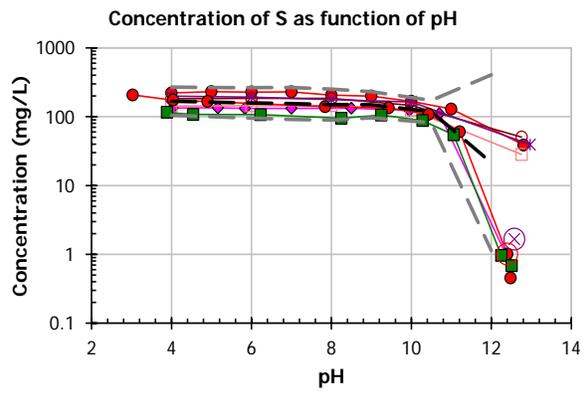
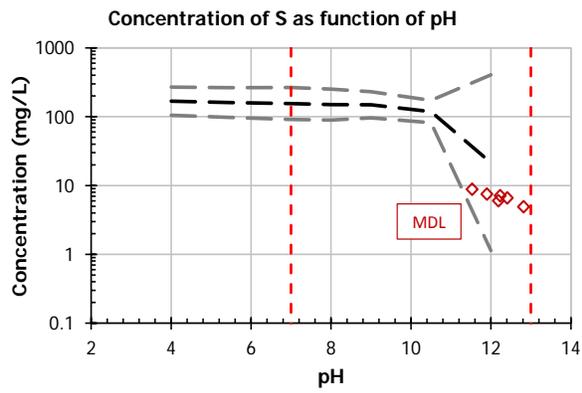
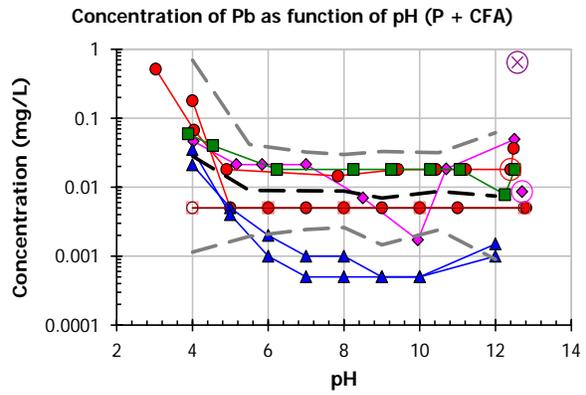
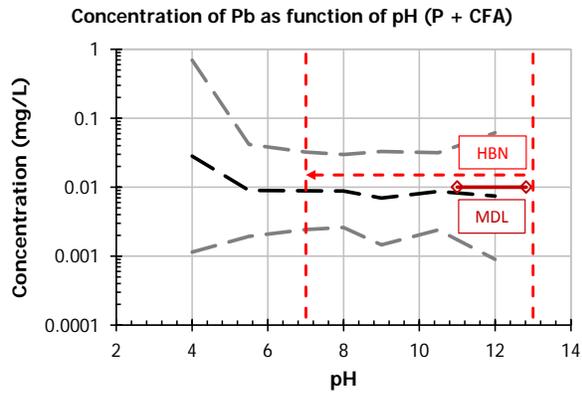
*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*



*The Impact of Coal Combustion Fly Ash Used as a Supplemental Cementitious Materials on The Leaching of Constituents from Cements and Concretes*

